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PHOTOGRAPHIC SCIENCE AND ENGINEERING
Volume 5, Number 4, July–August 1961

The Spectrophotometric Determination of Phenidone in Developers

HELEN M. ROSENBERGER, *Chemical Research and Engineering Department, A. B. Dick Co., Chicago, Ill.*

A rapid accurate spectrophotometric method for the determination of 1-phenyl-3-pyrazolidone (Phenidone) in concentrated liquid developers utilizes the maximum absorbance of a chloroform extract at 250 mμ. The procedure provides speed of performance for control purposes and eliminates the preparation and standardization of reagent solutions.

Phenidone* (1-phenyl-3-pyrazolidone) has received considerable attention in recent years, primarily because of its use in conjunction with hydroquinone in concentrated liquid developers or monobaths.

Early published methods for the determination of Phenidone were based on iodometric determinations. The method of Axford[1] called for an addition of a known volume of iodine, not to exceed 5% in excess of the theoretical requirement, to an acidified sample of developer which had been boiled to remove sulfur dioxide. The excess iodine was back-titrated with sodium thiosulfate in the presence of starch. The accuracy of the method critically depended upon the excess of iodine and therefore left considerable margin for error when the Phenidone concentration of the sample was unknown.

Levenson and Rumens,[2] by introducing a chloroform extraction of the Phenidone at pH 8 and other modifications, decreased the dependency upon the excess of iodine. By their modifications, the iodine excess could be between 40 and 200% for a ±2% accuracy. This allowed for considerable latitude when the Phenidone concentration was unknown and gave fairly reproducible results. However, the method was not found to be completely satisfactory for developers which contained thiosulfate ions.

Van Veelen and Ruysschaert[3] have recently published a method based on the infrared absorption at 5.85 μ of a chloroform extract of the developer. The analytical data presented indicates an estimated standard deviation of 0.076 for a Phenidone concentration of 2.0 grams/liter. The use of an instrumental method is certainly advantageous from the standpoint of time and the elimination of standardizing solutions, but for quantitative infrared determination, it is desirable to have the ease of performance provided by a double-beam spectrophotometer. In some production or quality control laboratories where such an instrument is not always available, however, an instrument for the ultraviolet working range usually may be found.

The ultraviolet spectrum of Phenidone in chloroform (Fig. 1) exhibits a strong absorption at 250 mμ attributed to the C=O chromophore. Work in this laboratory showed that the 250-mμ absorption peak obeyed Beer's law in the concentration investigated (from 0.1 to 3.5 mg Phenidone per 100 cc chloroform) and was used for the quantitative determination of Phenidone. This provided a sufficient working range, since the concentration of Phenidone in most concentrated liquid developers is from 1 to 3 grams/liter.

Experimental Procedure

1. A Beckman Model DU spectrophotometer, equipped with 10-mm silica cells, a hydrogen discharge tube, and a DU power supply was used for all absorbance measurements.

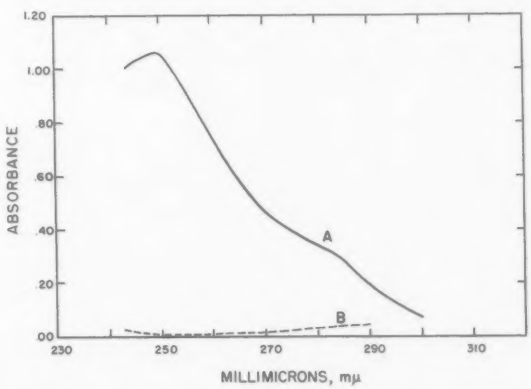

Fig. 1. Curve A, ultraviolet spectrum of 2 mg Phenidone per 100 cc chloroform, cell thickness, 10 mm. Curve B, spectrum of typical "blank" extract; cell thickness, 10 mm.

Received 10 March 1961; revised 26 April 1961.

* Registered trademark.

1. A. J. Axford, *Phot. Eng.*, 7: 23 (1956).
2. G. I. P. Levenson and M. G. Rumens, *J. Phot. Sci.*, 7: 38 (1959).
3. G. F. Van Veelen and H. Ruysschaert, *Phot. Sci. & Eng.*, 4: 129 (1960).

2. A standard solution was prepared from photographic grade Phenidone in U.S.P. chloroform. Aliquots containing 0.1 to 3.5 mg/100 cc chloroform were prepared, and a straight-line calibration curve was obtained by plotting absorbance against concentration.
3. *Spectrophotometric Procedure:* Introduce a 1-cc sample into a 250-cc separatory funnel by means of a pipette. Add 90 cc distilled water, a few drops of phenolphthalin indicator, and 20% sulfuric acid dropwise until the solution is decolorized. Add 50 cc chloroform, stopper funnel, and shake for 1 min. Allow the layers to separate and collect the chloroform layer in a 100-cc volumetric flask. Repeat the extraction with 40 cc chloroform, add this extract to the volumetric flask and dilute to the mark with chloroform.

   The absorption of the sample is measured in a 10-mm silica cell at 250 mμ against chloroform. The concentration of Phenidone is read from the calibration curve.

Discussion of Results

The method was evaluated by measuring the Phenidone content of carefully prepared synthetic solutions. The composition of the solutions in grams per liter is shown in Table I.

Four separate determinations were made on each solution and the results are shown in Table II. The over-all accuracy of the method is reflected in the averaged estimated standard deviations of 0.053 over a range of samples having a Phenidone content of 1 to 2.6 grams/liter.

TABLE I. Composition of Test Solutions

	Solution number			
	1	2	3	4
Phenidone	1.03	1.45	2.01	2.56
Hydroquinone	23.49	15.60	29.91	20.94
Sodium sulfite	117.33	115.47	143.12	133.51
Sodium thiosulfate	10.83	——	11.36	18.11
Potassium bromide	1.06	1.85	1.32	1.39
Sodium hydroxide	21.56	15.37	20.06	25.32

TABLE II. Analytical Results on Test Solutions
Phenidone concentration in grams per liter

Solution number	Present	Found	Mean $\bar{X}$	Est. std. dev.*
1	1.03	1.03	1.02	0.017
		1.00		
		1.04		
		1.01		
2	1.45	1.45	1.45	0.055
		1.36		
		1.50		
		1.50		
3	2.01	1.98	1.97	0.071
		1.95		
		1.91		
		2.04		
4	2.56	2.49	2.51	0.068
		2.60		
		2.43		
		2.50		

* $s = [\Sigma(X - \bar{X})^2/(n-1)]^{1/2}$

TABLE III. Effect of Aeration

Hours of oxidation	Phenidone, mean $\bar{X}$, g/l
0	1.45
2	1.43
7	1.42
24	1.40

The method described has only been utilized for the determination of Phenidone in monobaths of the general formulas cited. However, it should be applicable to all Phenidone developers providing no other products containing the carbonyl group are present.

The oxidation product of Phenidone does not exhibit a C=O band[3] and therefore does not interfere with the measurement of Phenidone in aged developers. Phenidone is quantitatively regenerated by hydroquinone[4] in fresh Phenidone-hydroquinone developers and in oxidized developers where hydroquinone and sodium sulfite are present in sufficient quantity. The effect of air oxidation was demonstrated by maintaining solution No. 2 at 25° ± 1°C and bubbling air through it. Phenidone was determined at intervals, and the data are shown in Table III.

The effect of background absorption was determined by preparing synthetic mixtures containing all of the developer components except the Phenidone. These were extracted in the manner described and the absorptions were measured (Fig. 1). The absorptions were negligible and the maximum deviation reflected in the theoretical Phenidone content was 0.05 grams/liter in a mixture where the hydroquinone had been increased to 40 grams/liter. Therefore, the use of chloroform as a blank should provide sufficient accuracy for most practical applications of the method.

Since completion of this investigation, a paper by Tojo *et al*[5] has appeared which also describes an ultraviolet determination of Phenidone. Tojo extracts with chloroform at pH 5–6 and then washes the extract with dilute sodium bicarbonate solution to remove the interfering sulfur dioxide formed by acidification of sulfite-containing developers. Performing the extraction well above pH 8, as described in the method presented here, prevents formation of sulfur dioxide and obviates washing the extract.

The author is grateful to Dr. Clarence J. Shoemaker for his encouragement of this project and to the A. B. Dick Co. for permission to publish this work.

4. A. J. Axford and J. D. Kendall, *Proc. Roy. Phot. Soc. Conference*, London, 1953, p. 169.
5. Ei Tojo, Kazuo Kurosaki, and Mitsuo Ozawa, *J. Soc. Sci. Phot Japan*, **23**: 123 (1960).

PHOTOGRAPHIC SCIENCE AND ENGINEERING
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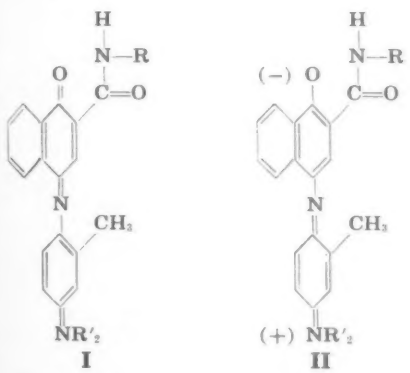
Indoaniline Dyes: IV.* Some Dyes Derived from 1-Hydroxy-2-Naphthamides

C. R. Barr, G. H. Brown, J. R. Thirtle, and A. Weissberger,
Research Laboratories, Eastman Kodak Company, Rochester, N.Y.

1-Hydroxy-2-naphthamides and 1-hydroxy-2-naphthanilides have been prepared and converted to indoaniline dyes by oxidative coupling with a *p*-phenylenediamine. In the dyes prepared, it has been observed that structural changes which favor charge separation in the dye molecule cause the absorption to be shifted to longer wavelengths; structural changes which inhibit charge separation cause hypsochromic shifts.

1-Hydroxy-2-naphthamides are widely used as couplers in chromogenic color photography to form indoaniline dyes by oxidative condensation with *p*-aminodialkylanilines.[1] We have studied the effect of structural changes on the absorption of these dyes. Variations in the amide moiety are most readily made and are described in the present paper; a study of the effect of substituents in the naphthol nucleus will be reported later. Our data are consistent with those of other investigations of similar compounds.[2]



I II

As in the case of the indoaniline dyes derived from phenols,[3] the two most important structures contributing to the resonance hydrid of the dye are the uncharged structure, I, and the ionic structure, II.

Communication No. 2133 from the Kodak Research Laboratories. Received 19 April 1961.

* For *Indoaniline Dyes. III*, see P. W. Vittum and G. H. Brown, *J. Am. Chem. Soc.*, **71:** 2287 (1949).

1. R. Fischer and H. Siegrist, *Phot. Korr.*, **51:** 18 (1914).
P. W. Vittum and A. Weissberger, *J. Phot. Sci.*, **2:** 81 (1954).
2. B. S. Portnaya, I. I. Levkoev, and N. S. Spasokukotskiĭ, *Doklady Akad. Nauk SSSR*, **82:** 603 (1952).
N. S. Spasokukotskiĭ, I. I. Levkoev, and B. S. Portnaya, *ibid.*, **93:** 671 (1953).
B. S. Portnaya, N. S. Spasokukotskiĭ, N. F. Turitsyna, T. P. Bobkova, G. I. Arbuzov, and I. I. Levkoev, *J. Gen. Chem. USSR*, **26:** 2537 (1956).
N. F. Turitsyna, B. S. Portnaya, N. S. Spasokukotskiĭ, T. P. Bobkova, G. I. Arbuzov, and I. I. Levkoev, *ibid.*, **26:** 2546 (1956).
3. P. W. Vittum and G. H. Brown, *J. Am. Chem. Soc.*, **68:** 2235 (1946); *ibid.*, **69:** 152 (1947).

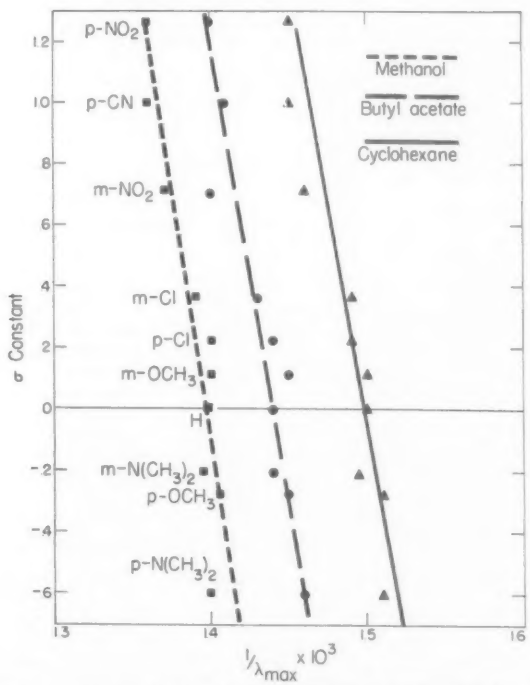
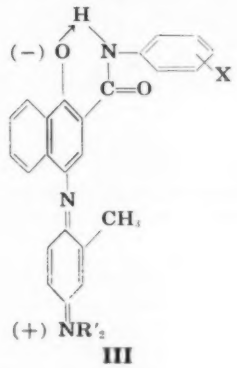


Fig. 1. Relation between λ_{max} and Hammett's σ-constants for *m*- and *p*-substituents on anilide ring of dyes derived from 1-hydroxy-2-naphthanilides.

Changes which increase the stability of **II** cause bathochromic shifts in agreement with the expectation that the contribution of **II** to the excited state would be greater than its contribution to the ground state. In Tables I and II are listed the values for the absorption maxima and the extinction coefficients of the dyes in cyclohexane, *n*-butyl acetate, and methanol. The corresponding data in methanol for the desmethyl dyes prepared by us or reported in the literature[2] are given in footnotes; the bathochromic shift in absorption maxima caused by the methyl group is consistent with published data for analogous dyes.[4]

An increase in polarity of the solvent promotes the contribution of Structure **II** and therefore gives rise to a bathochromic shift accompanied by an increase in molar extinction coefficient. Similarly, the greater the ability of the NHR-moiety of the amide to accept electrons, the greater is the bathochromic shift. This is illustrated by the series in which R is methyl, benzyl, and phenethyl and by the fact that a straight-line relationship is observed in a plot of Hammett's σ-constants for substituted aromatic primary amines against reciprocals of the λ_{max} values for the corresponding 1-hydroxy-2-naphthanilide indoaniline dyes (Fig. 1). These effects are probably related to the degree to which hydrogen-bonded structures such as **III** are favored.[5]



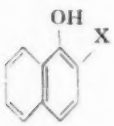
III

In the particular cases of the substituted anilides described here, strong electron-attracting substituents (+ σ-constants), by stabilizing this chelation,

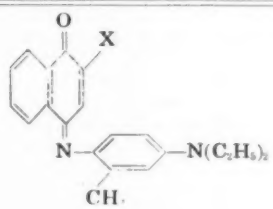
4. S. Hünig and P. Richters, *Ann. Chem.*, **612:** 282 (1958).

5. Evidence for such hydrogen-bonding has been reported by G. D. Bagratishvili, D. N. Shigorin, and N. S. Spasokukotskiĭ, *Zhur. Fiz. Khim. (USSR)*, **28:** 2185 (1954).

TABLE I. Couplers and Dyes Derived from 1-Hydroxy-2-Naphthamides



Couplers



Dyes

No.	X	Couplers: mp, deg C	Couplers: Recrystn. solvent	Dyes: mp, deg C	Dyes: Recrystn. solvent	Dyes: λ_{max}, mμ ($E \times 10^{-4}$): Cyclohexane	Butyl acetate	Methanol
1	$CONH_2$	191–192[a]	Ethanol	216–217	Ethanol	650 (—)[b]	671 (2.8)	693[c] (3.0)
2	$CONHCH_3$	123–124	Ligroin-benzene	114–115	Benzene	648 (2.7)	667 (2.9)	695 (3.0)
3	$CONHC_2H_5$	148–150[d]	Benzene	130–131	Cyclohexane	650 (2.7)	668 (2.8)	700[e] (2.9)
4	$CONHC_3H_7$-*i*	86–87	Ligroin	124–125	Carbon tetrachloride	650 (2.8)	675 (2.9)	700 (3.1)
5	$CONHC_4H_9$-*n*	69–70	Ligroin	94–95	Ligroin	648 (2.8)	670 (2.9)	697 (3.2)
6	$CONHC_4H_9$-*t*	115–117	Methanol	199–200	Ethyl acetate	650 (2.6)	675 (2.8)	700 (3.0)
7	$CONHC_5H_{11}$-*n*	58–60	Pet. ether	100–101	Cyclohexane	650 (2.7)	675 (3.0)	700 (3.2)
8	$CONC_6H_{11}$-*cyclo*	142–143	Ligroin	160–161	Ethanol	646 (2.7)	669 (2.9)	696 (3.1)
9	$CONHCH_2C_6H_5$	121–122	Ligroin	136–137	Ethyl acetate	653 (2.9)	675 (3.0)	700 (3.2)
10	$CONH(CH_2)_2C_6H_5$	125–126	Benzene-pet. ether	111–112	Ethanol	650 (2.9)	673 (3.0)	697 (3.2)
11	$CON(CH_3)_2$	114–115	Acetone-water	181–182	Ethanol	615 (1.8)	628 (2.0)	664 (2.2)
12	CON satd O	132	Ethanol	163–164	Ethanol	618 (2.0)	625 (2.0)	661 (2.3)

a. Lit. mp, 191–192° (Ref. 7); 190° (Ref. 8); 202° (Ref. 9).
b. Low solubility.
c. Desmethyl, 672 mμ (Ref. 7).
d. Lit. mp, 152° (Ref. 7).
e. Desmethyl 672 mμ (Ref. 7).

7. B. S. Portnaya, N. S. Spasokukotskiĭ, N. F. Turitsyna, T. P. Bobkova, G. I. Arbuzov, and I. I. Levkoev, *J. Gen. Chem. USSR*, **26:** 2537 (1956).
8. H. Meyer, *Monatsh. Chem.*, **22:** 790 (1901).
9. R. Anschütz and K. Runkel, *Ann. Chem.*, **346:** 361 (1906).

aid the charge separation. The energy required for excitation is thereby reduced, and bathochromic shifts of the dyes are observed. Conversely, substituents with negative σ-constants do not favor chelation, and hypsochromic shifts result. Replacement of the hydrogen of the amide by an alkyl group causes a large hypsochromic shift because hydrogen-bonding is no longer possible.

Experimental

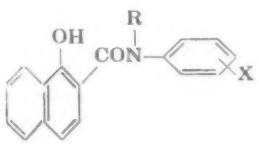
Preparation of the Amides. The amides were prepared by reaction of the appropriate amine or aniline with phenyl 1-hydroxy-2-naphthoate or with 1-hydroxy-2-naphthoyl chloride. The recrystallization solvent is indicated in the tables.

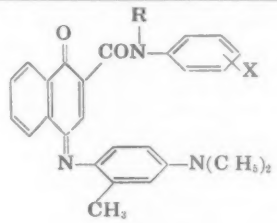
Preparation of the Dyes. The dyes were prepared by Method A of an earlier paper from these Laboratories.[6] All analyses were within acceptable limits of error, ±0.3% absolute, and are not reported here.

Spectrophotometric Measurements. The dyes were dissolved in specially purified methanol to make 4×10^{-5} *M* solutions which were read in 1-cm cells, using the General Electric Automatic Recording Spectrophotometer.

6. G. H. Brown, J. Figueras, R. J. Gledhill, C. J. Kibler, F. C. McCrossen, S. M. Parmerter, P. W. Vittum, and A. Weissberger, *J. Am. Chem. Soc.*, **79:** 2919 (1957).

TABLE II. Couplers and Dyes Derived from 1-Hydroxy-2-Naphthanilides





	Couplers				Dyes				
							λ_{max}, mμ ($E \times 10^{-4}$)		
No.	R	X	mp, deg C	Recrystn. solvent	mp, deg C	Recrystn. solvent	Cyclohexane	Butyl acetate	Methanol
1	H	H	155–156[a]	Benzene	205–206	Ethyl acetate	665 (3.3)	694 (3.4)	712[b] (3.6)
2	CH_3	H	124–126[c]	Ligroin	188–189	Ethanol	609 (1.7)	629 (1.9)	662[d] (2.1)
3	C_6H_5	H	144–145[e]	Ethanol	153–154	Ethanol	609 (1.3)	628 (1.4)	666[f] (1.6)
4	H	*o*-$N(CH_3)_2$	96–98[g]	Ligroin	173–176	Ethanol	663 (3.0)	689 (3.2)	714[h] (3.3)
5	H	*m*-$N(CH_3)_2$	172–173[i]	Ligroin-benzene	195–196	Ethanol	669 (2.9)	694 (3.4)	719[j] (3.5)
6	H	*p*-$N(CH_3)_2$	167–168[k]	Ligroin-benzene	201–202	Acetone	664 (3.1)	687 (3.3)	712[l] (3.4)
7	H	*o*-OCH_3	161–162[m]	Benzene	203–204	Ethyl acetate	658 (3.1)	682 (3.3)	714 (3.5)
8	H	*m*-OCH_3	138–139	Benzene	172–173	Benzene	666 (3.2)	691 (3.4)	712 (3.6)
9	H	*p*-OCH_3	129–130[n]	Benzene	185–186	Benzene	662 (3.1)	689 (3.3)	711 (3.5)
10	H	*o*-Cl	163–164[o]	Ligroin-benzene	198–199	Ethyl acetate	666 (3.2)	693 (3.4)	718[p] (3.6)
11	H	*m*-Cl	182–183[q]	Benzene	174–175	Benzene	675 (3.4)	700 (3.5)	720[r] (3.7)
12	H	*p*-Cl	174–175[s]	Benzene	200–201	Benzene	671 (3.5)	697 (3.5)	716[t] (3.6)
13	H	*p*-CN	196–198	Ethanol	227–228	Benzene	688 (—)[u]	711 (3.8)	733 (3.9)
14	H	*p*-SO_2NH_2	275–276	Toluene	198–199	Acetone	—[u] (—)[u]	705 (3.6)	725 (3.7)
15	H	*o*-NO_2	203–204[v]	Benzene	212–213	Benzene	670 (—)[u]	700 (3.3)	725[w] (3.5)
16	H	*m*-NO_2	251–252[x]	Dioxane	188–189	Carbon tetrachloride	687 (2.6)	712 (2.8)	731[y] (—)[u]
17	H	*p*-NO_2	243–244[z]	Chlorobenzene	208–209	Acetone	688 (3.8)	713 (3.9)	729[aa] (3.8)
18	H	2,4,6-CH_3	152–154	Ethanol	187–188	Ethanol	659 (3.1)	681 (3.2)	707 (3.4)
19	H	2,4,6-Cl	209–210	Butanol	194–195	Ethanol	672 (3.2)	697 (3.5)	725 (3.6)

a. Lit. mp, 155–156° (Ref. 11).
b. Desmethyl, 690 mμ, lit. 692mμ (Ref. 7).
c. Lit. mp, 136° (Ref. 7).
d. Desmethyl, lit. 640 mμ (Ref. 7).
e. Lit. mp, 154° (Ref. 7).
f. Desmethyl, lit. 645 mμ (Ref. 7).
g. Lit. mp, 110–111° (Ref. 10).
h. Desmethyl, 686 mμ, lit. 687 mμ (Ref. 10).
i. Lit. mp, 173° (Ref. 10).
j. Desmethyl, 693 mμ, lit. 691 mμ (Ref. 10).
k. Lit. mp, 173–174° (Ref. 10).
l. Desmethyl, lit. 690 mμ (Ref. 10).
m. Lit. mp, 161–162° (Ref. 11).
n. Lit. mp, 129–130° (Ref. 11).
o. Lit. mp, 160–162° (Ref. 10).
p. Desmethyl, lit. 696 mμ (Ref. 10).
q. Lit. mp, 179–180° (Ref. 10).
r. Desmethyl, lit. 697 mμ (Ref. 10).
s. Lit. mp, 172–173° (Ref. 10).
t. Desmethyl, lit. 696 mμ (Ref. 10).
u. Low solubility.
v. Lit. mp, 200–201° (Ref. 10).
w. Desmethyl, 696 mμ, lit. 696 mμ (Ref. 10).
x. Lit. mp, 242° (Ref. 10).
y. Desmethyl, 700 mμ, lit. 698 mμ (Ref. 10).
z. Lit. mp, 241° (Ref. 10).
aa. Desmethyl, lit. 705 mμ (Ref. 10).

10. N. F. Turitsyna, B. S. Portnaya, N. S. Spasokukotskiĭ, T. P. Bobkova, G. I. Arbuzov, and I. I. Levkoev, *J. Gen. Chem. USSR*, **26:** 2546 (1956).

11. G. V. Jadhav S. N. Rao, and N. W. Hirwe, *J. Univ. Bombay*, **5:** 137 (1936).

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Organic Silver-Complexing Agents for Photographic Monobaths

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Six classes of organic silver-complexing agents have been studied for possible use in photographic monobaths. Data include film-clearing times as a function of pH and temperature. A comparison is made of the photographic characteristics of monobaths containing either an organic or an inorganic silver-complexing agent.

In 1889 in England, W. D. Richmond[1] added sodium thiosulfate and ammonium thiocyanate in equal gram-quantities to a pyrogallol–ammonia developer to make the world's first impractical monobath. Although he called the process "concurrent development and fixation," Richmond did state that it was impractical when compared to the conventional processing of that time. The term "monobath" has now come to include the solution made by Richmond as well as all other single-solution developer-fixers.

During the seventy years since Richmond's initial experiment, many practical photographic chemists have striven to overcome the degrading effects of adding a silver-complexing agent to a developer. Such developer-fixers usually resulted in a severe loss in emulsion speed of photographic materials as well as reduced contrast and lowered maximum densities. To overcome the loss in photographic characteristics, the pH of the monobath was usually increased, thus adding softened emulsion layers and solution-instability to the list of processing difficulties.

Besides the practical formulation of monobaths, some consideration has been given by other investigators to the more fundamental aspects of development in solutions of high silver halide solvency. Richmond[1] himself recognized that ". . . development goes on after fixation has been effected. . . ." In 1953, Clarke, Milner, and Gomez-Ibanez[2] compared developed density with silver analysis to show that physical development was playing an important role in image formation, resulting in more silver being formed at low-level exposures by the monobath processing than that by a low-solvent developer. More recently, Klein[3,4] and also Eggenschwiller and Jaenicke[5] have studied the role played by chemical and physical development in developing solutions of high solvency for the silver halide.

All of these practical and theoretical aspects of monobath processing have been concerned with inorganic silver-complexing agents, usually sodium thiosulfate. In a comprehensive two-part survey of the seventy years of monobath formulation, Newman[6] cited only three references to monobaths containing organic compounds as the silver-complexing agent. Mercaptopyridines or pyrimidines were disclosed by Dreywood[7] in a U.S. Patent. In 1956, Haist, King, Rasch, and Crabtree[8] published information on highly acid titanium monobaths containing mercaptosuccinic acid. In 1957, a British patent by Wenske and Warnke[9] claimed the use of thiourea, either alone or in combination with sodium thiosulfate. Issued shortly after the publication of Newman's 1959 survey was a pertinent U.S. Patent by Haist and King[10] disclosing the use of monothioglycerol, 2-thiobarbituric acid, and the β-mercaptoethylamines in 1-phenyl-3-pyrazolidone–ascorbic acid monobaths.

With the exception of the Haist, King, Rasch, and Crabtree paper and the three patents mentioned, there does not appear to be any other publication concerned with monobaths containing organic sulfur-complexing agents for silver. It was of interest, therefore, to compare the clearing characteristics of a number of commercially available organic silver-complexing compounds with those of sodium thiosulfate, and to study practical monobath systems with some of these agents.

Film-Clearing Procedure

Stock solutions with a concentration of 0.25 molar of the compound to be tested were made at pH values of 10.5 and 12.0. In certain cases, where the compound

Communication No. 2146 from the Kodak Research Laboratories. Presented at the 1960 Rapid Processing Symposium, Washington, D.C., 15 October 1960. Received 20 January 1961.

1. W. D. Richmond, *Brit. J. Phot.*, **36:** 827–828 (1889).
2. R. G. Clarke, C. E. Milner, Jr., and J. Gomez-Ibanez, *Phot. Eng.*, **4:** 231–235 (1953).
3. E. Klein, *Z. Elektrochem.*, **62:** 505–519 (1958).
4. ———, *J. Phot. Sci.*, **8:** 178–182 (1960).
5. H. Eggenschwiller and W. Jaenicke, *Phot. Korr.*, **95:** 149–159 (1959).
6. A. A. Newman, *Brit. J. Phot.*, **106:** 44–48, 56, 66–68 (1959).
7. R. P. Dreywood, U. S. Pat. 2,525,532 (1950).
8. G. M. Haist, J. R. King, A. A. Rasch, and J. I. Crabtree, *Phot. Eng.*, **7:** 182–189 (1956).
9. K. Wenske and A. Warnke, Brit. Pat. 768,401 (1957).
10. G. M. Haist and J. R. King, U. S. Pat. 2,875,048 (1959).

Fig. 1. Automatic vertical agitator with the constant-temperature water bath removed.

had effective clearing characteristics at a lower pH, a stock solution of 0.25 molar of the compound was made at pH 6.5. The pH values were adjusted with sodium hydroxide. The use of other compounds and buffering agents was avoided because often the presence of salts had a significant effect on the clearing times of certain silver-complexing compounds.

A 30-ml portion of the stock solution was used for each clearing-time determination. The sample temperature was maintained by a constant-temperature water bath, the tank being made of clear plastic for observation purposes. Temperatures were studied from 55° to 135°F, usually in 15° increments throughout this range. Temperatures were maintained at less than ±1°F maximum deviation.

Kodak Fine Grain Positive Film was used for all clearing-time determinations. Dry film was used to simulate monobath processing conditions. Standardized agitation was supplied by an automatic vertical agitator (AVA). In Fig. 1, the constant-temperature water bath has been removed for a better pictorial presentation of the details of the agitator. The horizontal arm can be raised so that as many as five film strips can be attached. When the arm is lowered so that it comes into contact with the central fulcrum, the microswitch simultaneously starts the timing clock and the vertical agitator. Two up-and-down cycles, each of the four strokes being ½ in. long, are completed each second.

A precise method for determining the exact clearing time was followed, simulating in some degree the split-field techniques of photometry. The film strip was first lowered into the solution so that the top ¼ in. of the total eventual immersion depth was not in solution. After a short time interval, the AVA was started. The pretreated part of the film strip cleared first since it had been immersed the longest time. The clearing time was taken at the moment when the dividing line between the cleared area and the top area disappeared. Since the observation of the clearing time was done visually in the testing procedure, only compounds that formed clear silver complexes could be tested.

Clearing-Test Results

Thiosulfates have been the established silver-complexing agents in use for many years in acid fixing baths and other solutions. More recently, the thiosulfates have been utilized in the alkaline processing solutions of the diffusion-transfer systems, and now commercial monobaths for film and paper processing at conventional temperatures are available. The clearing curves for Fine Grain Positive Film in a solution containing 0.25 *M* sodium thiosulfate at pH's of 6.5, 10.5, and 12.0, and the clearing curves for 0.25 *M* ammonium thiosulfate under the same test conditions are shown in Fig. 2. The clearing characteristics of both of these thiosulfate salts are relatively independent of pH but at 70°F the ammonium salt required only half the time that the sodium salt needed to clear. Increasing the temperature resulted in a shorter clearing time with either salt, and the ammonium salt still was the significantly faster of the two.

Mercaptoacetic acid is an example of a simple mercapto acid whose clearing characteristics are dependent upon pH. Raising the temperature resulted in a shorter time to clear but maintained essentially the same time differential between the two pH values. The pH effect with this acid was the greatest of any compound tested in this group of silver-complexing agents (Fig. 3).

Cysteine might also be called α-amino-β-mercaptopropionic acid, differing only from mercaptoacetic acid by the introduction of an aminomethylene group. The clearing curves for cysteine hydrochloride at pH's of 10.5 and 12.0 closely parallel each other over the temperature range studied (Fig. 3). Cysteine

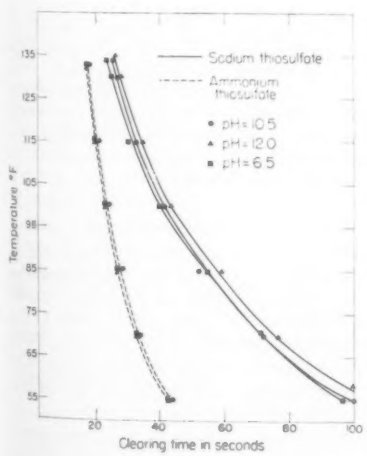

Fig. 2 (left). Effect of temperature and pH on film-clearing time.

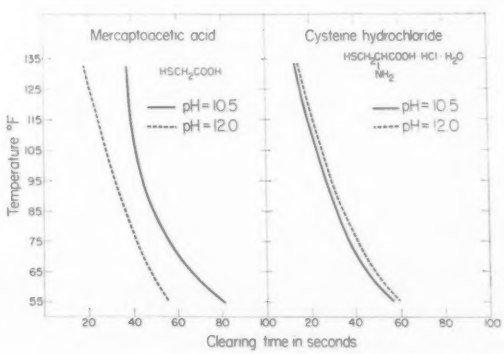

Fig. 3 (right). Effect of temperature and pH on film-clearing time.

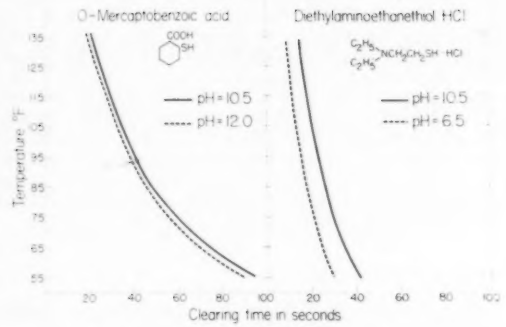

Fig. 4. Effect of temperature and pH on film-clearing time.

hydrochloride is more effective than mercaptoacetic acid at all temperatures at pH 10.5 and at the higher temperatures at pH 12.0.

o-Mercaptobenzoic acid (often called thiosalicylic acid) showed a considerable decrease in clearing time with increasing temperature (Fig. 4). At pH 10.5, the clearing time of Fine Grain Positive Film dropped from 95 sec at 55°F to 20 sec at 135°F. There was not much variation in the clearing time at the two pH values tested, however.

2-Diethylaminoethanethiol hydrochloride formed an opaque silver complex at high pH but cleared Fine Grain Positive at pH 10.5 and 6.5 (Fig. 4). This compound was appreciably more active at the lower pH, the time to clear dropping from 33 sec at 55°F to 9 sec at 130°F.

Monothioglycerol does not clear Fine Grain Positive below pH 9.0 but is effective in the alkaline region above that pH (Fig. 5). The activity of this compound at pH 10.5 and 12.0 was very similar. The clearing time decreased from 46 sec at 55°F to 15 sec at 130°F. This temperature effect was not as great as with some of the other compounds tested.

The action of thiourea upon Fine Grain Positive at pH values of 6.5 and 10.5 is shown in Fig. 5. Higher pH solutions could not be used because of the fogging properties of thiourea for photographic film.

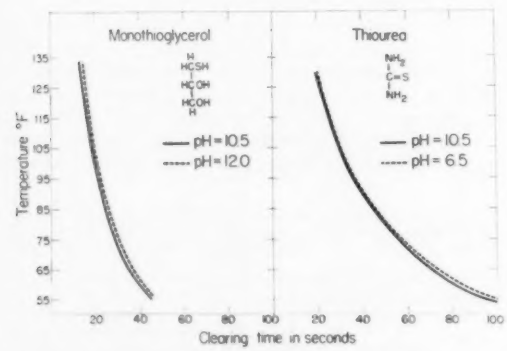

Fig. 5. Effect of temperature and pH on film-clearing time.

TABLE I. Clearing Times, in Seconds, of Kodak Fine Grain Positive Film

	pH 6.50		pH 10.50		pH 12.0	
	70°F	130°F	70°F	130°F	70°F	130°F
Sodium thiosulfate	72	25	73	27	79	28
Ammonium thiosulfate	35	18	33	18	34	18
Mercaptoacetic acid	—	—	65	38	43	20
Cysteine hydrochloride	—	—	44	15	48	17
o-Mercaptobenzoic acid	—	—	66	23	63	22
2-Diethylaminoethanethiol hydrochloride	24	9	34	15	—	—
Monothioglycerol	—	—	33	14	34	15
Thiourea	65	19	63	19	—	—

The clearing curves at these two pH values are almost identical. The effect of increased temperature was large, reducing the film-clearing time from 100 sec at 55°F to 19 sec at 130°F.

A summary of the clearing times of Fine Grain Positive for all the compounds will be found in Table I. These times are valid only for the conditions of this study. It is hoped, however, that the relative activity of the clearing agents might be retained under different conditions of usage, and thus the curves and table should be useful as a starting point in the formulation of photographic solutions that require silver-complexing agents to be present.

Monobath Procedures

Kodak Verichrome Pan Film was used exclusively in the processing tests made. A monobath containing sodium thiosulfate as the silver-complexing agent and another monobath with mercaptoacetic acid were both formulated to match the sensitometric characteristics of Verichrome Pan Film processed for 8½ min at 68°F in an experimental Metol–hydroquinone developer. The MQ developer is of conventional composition and produced sensitometric results similar to those of D-76 developer. The film was immersed at the beginning of the processing period and removed at the end of the period without either the film or the solution being disturbed during the processing. This procedure was chosen to simulate the treatment given in the Pako Filmachine. Mercaptoacetic acid was chosen for one of the monobaths because it is a readily available, inexpensive mercapto compound. The formula for each experimental monobath is as follows:

Sodium Thiosulfate Monobath

Water	750.0	ml
1-Phenyl-3-pyrazolidone	4.0	grams
Hydroquinone	12.0	grams
Sodium sulfite (anhydrous)	50.0	grams
Sodium thiosulfate, pentahydrate	110.0	grams
Sodium hydroxide	4.0	grams
Water to make	1.0	liter

pH = 10.3

Dissolve the chemicals in the order listed.

Mercaptoacetic Acid Monobath

Water	750.0	ml
1-Phenyl-3-pyrazolidone	5.0	grams
Sodium isoascorbate	24.0	grams
Sodium sulfite (anhydrous)	48.0	grams
Mercaptoacetic acid, sodium salt	24.0	grams
2-Diethylaminoethanol	80.0	ml
Mucic acid	1.2	grams
Potassium hydroxide	12.0	grams
2-Anthraquinone sulfonate, sodium salt	0.25	gram
Water to make	1.0	liter

pH = 10.7

Dissolve the chemicals in the order listed.

The processing time was 6 min at 75°F, with intermittent agitation which required raising and lowering the film strip once each minute. The film strips were washed for 10 min and dried in air at room temperature.

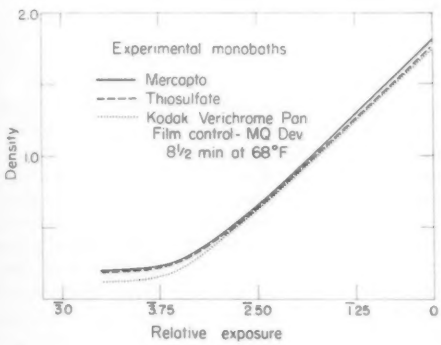

Fig. 6. Image densities produced by conventional development and monobath processing.

Monobath Results

The two monobaths have image-density curves that are a close match for conventional development of Verichrome Pan Film. The fog level for the two monobaths is higher (Fig. 6), however, but no great effort was made to complicate further the monobath formulas by adding specific agents that might exert control over the fog density. When silver, determined by x-ray spectrometric analysis, is plotted against relative exposure (Fig. 7), the curves for the three processing solutions are no longer similar. Both monobaths have produced more silver in the low-exposure areas than did the developer. Actually, the thiosulfate monobath has given more developed silver than has the MQ developer, except at the highest exposures.

For an ideal comparison of a mercaptoacetic acid and the sodium thiosulfate monobaths, it would have been desirable to have identical formulas for each one, except for the silver-complexing agent. This was not possible. The reason for the greater complexity of the mercaptoacetic acid monobath is indicated by the following experiments: Mercaptoacetic acid of the concentration present in the monobath was dissolved in water adjusted to the alkalinity of

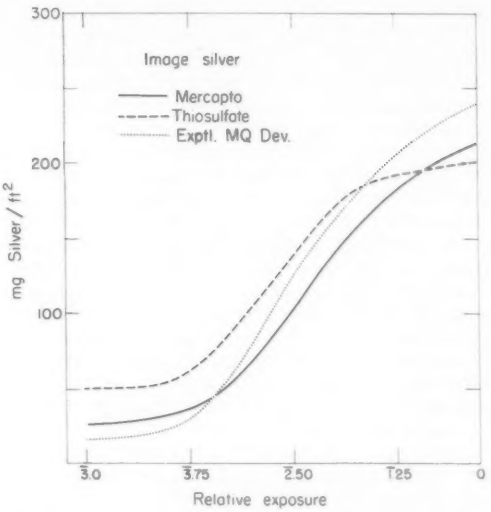

Fig. 7. Image silver produced by conventional development and monobath processing.

the monobath. Similarly, the monobath concentration of sodium thiosulfate was dissolved in water adjusted to the pH of the thiosulfate monobath. The mercaptoacetic acid solution (Curve A, Fig. 8) cleared the film faster than the thiosulfate solution (Curve B, Fig. 8) at all temperatures from 55° to 125°F, although the differences in clearing time were much less at the higher temperatures. Agitation for these clearing tests was the same as that used for the regular monobath processing. At 70°F, the film

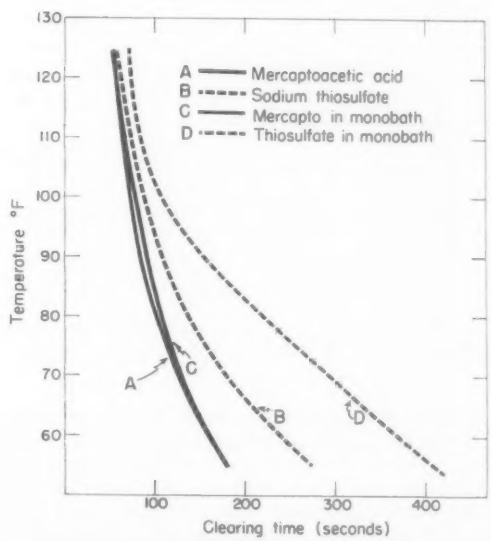

Fig. 8. Clearing times of silver-complexing agents alone (Curves A and B) and in monobath formulations without developing agents (Curves C and D).

was cleared in 125 sec by the mercaptoacetic acid and in 180 sec by the thiosulfate solution.

Clearing time was also studied by using the full monobath composition of each monobath with the developing agents omitted from each bath. The mercaptoacetic acid was comparatively unaffected by the addition of the other components of the monobath, giving clearing times very similar to this agent alone (Curve C, Fig. 8). However, the clearing time was slowed considerably when the thiosulfate was in the presence of the other salts of its monobath (Curve D, Fig. 8). The mercaptoacetic monobath, without developing agents, cleared the film in 130 sec at 70°F but the thiosulfate monobath without developing agents required 300 sec to clear.

Because of this considerable difference in silver halide solvency, the mercaptoacetic acid monobath must have a more rapid developing action in order to ensure sufficient developed density. This was achieved by the combination of 1-phenyl-3-pyrazolidone and sodium isoascorbate, the addition of 2-diethylaminoethanol, and a pH of 10.7. This monobath has a lower salt content and a higher pH than the thiosulfate monobath, so mucic acid was added as an antiswelling agent. The sodium salt of 2-anthraquinone sulfonate was added to control fog. The addition of a like amount of amine to the thiosulfate monobath had little effect on the density–relative exposure characteristic curve, producing increased fog densities without significant change in the densities of the rest of the curve.

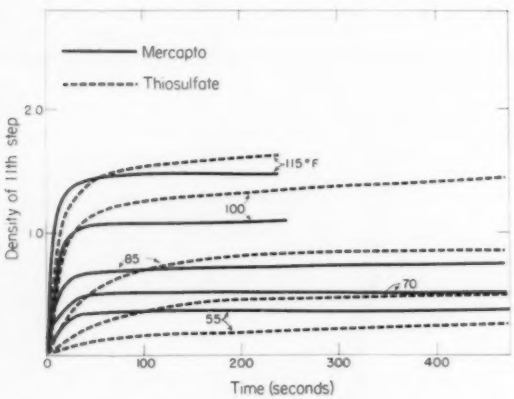

Fig. 9. Growth of 11th-step image densities with time for mercapto and thiosulfate monobath processing.

To study the growth of density during the processing cycle, film strips were processed for 30, 60, 120, 240, and 480 sec in the two monobaths, then stopped in 3% acetic acid, fixed, washed, and dried. Processing temperatures were 55°, 70°, 85°, 100°, and 115°F. Figure 9 graphically illustrates the growth of the optical density of the 11th-step exposure (log E = 2.25 mcs) with time at these temperatures for the two monobaths. Densities given by the mercaptoacetic acid monobath approach a maximum within 60 sec and do not increase after that time; densities produced by the thiosulfate monobath continue to show more growth throughout the entire time.

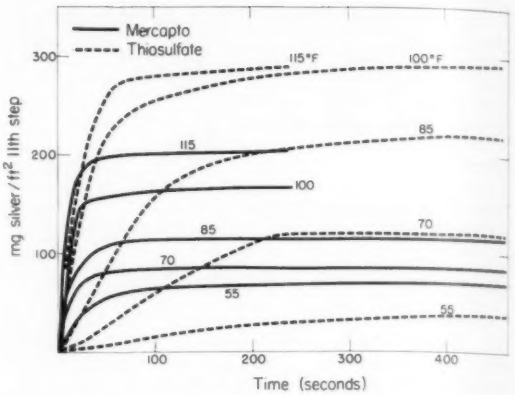

Fig. 10. Growth of 11th-step image silver with time for mercapto and thiosulfate monobath processing.

The silver content for each 11th-step exposure was determined by x-ray spectrometric analysis (Fig. 10). In the case of the mercaptoacetic acid monobath, the silver produced with time for the same range of temperatures as before shows a sharp initial rise, followed by a period of constant silver content. The thiosulfate bath again had a long period of increasing silver growth.

The covering power, that is, the ratio of the optical density to silver, of the 11th step is plotted against time for 70°F processing (Fig. 11). Because both density and silver were invariant after 30 sec, the mercaptoacetic acid monobath had constant covering-power values. But the covering power for the silver produced by the thiosulfate bath decreased steadily with time to low values.

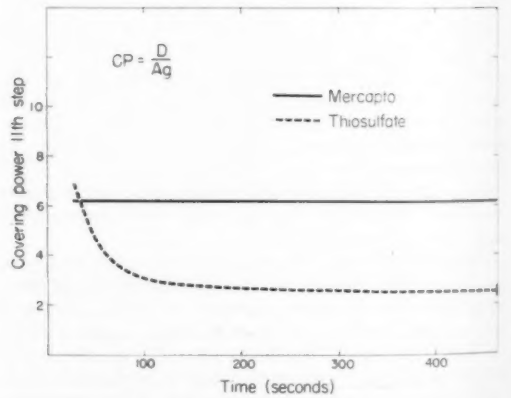

Fig. 11. Variation of covering power with time of processing in mercapto or thiosulfate monobaths.

Discussion

The study of clearing time as a function of temperature and pH has shown that there exist a considerable number of structurally different organic mercapto compounds that are capable of silver-complexing activity. Most of these compounds are suitable only for use in alkaline solution, such as for monobaths, but one compound of those shown, 2-diethylaminoethanethiol hydrochloride, is also very active under acid conditions. The actual choice of one of these compounds for practical use will also depend on other factors not discussed, such as cost, as well as odor, toxicity, and other characteristic properties.

Some of the photographic properties of the organic sulfur silver-complexing agents are shown by the specific comparison of a mercaptoacetic acid monobath with a similar sodium thiosulfate monobath. This organic agent was more rapid-acting than its inorganic counterpart, requiring a more potent developing action to give an equal density response. The presence of the rest of the salts of the monobath considerably slowed the action of the thiosulfate but this salt effect was not of appreciable importance with the organic compound in a monobath.

There does appear to be a very marked difference in the mechanism of action of the two types of monobaths. After a sharp initial rise, the growth of both image density and image silver is stopped in the monobath containing mercaptoacetic acid, but there is a continued growth of both of these with the thiosulfate bath, even after the film has been shown to have cleared. This continued growth is apparently the result of physical development of the dissolved silver salt upon filamentary silver of the image and other nuclei. Such growth results in the silver particles becoming more massive without a material increase in their projection area. This growth in silver without a like increase in optical density is evidenced in the steadily declining covering power with increasing time of action of the thiosulfate monobath. It is likewise evident that continued immersion of a silver image in a solution containing silver salt, as in a used thiosulfate monobath, will not be without effect, and will probably result in an increase of graininess of the silver image.

Although only one monobath based on a single organic silver-complexing agent has been discussed, there are a number of advantages of monobaths containing this and other mercapto compounds that the authors have observed during the formulation of baths for a variety of photographic films and papers. In general, this kind of monobath is free of the silver sludging that is so pronounced during high-temperature processing with thiosulfate monobaths, or is commonly observed after letting a used thiosulfate monobath stand in the stock bottle after processing. This freedom from silver sludging is due to the greater stability of the silver complex of the organic compound as compared to the stability of the inorganic complex.

Monobaths containing these organic agents can be formulated with very low salt content, permitting very rapid processing at high temperatures. Fog formation is suppressed by the more rapid action of the organic complexing agent, an especially valuable property at high temperatures. Mercapto compounds have antioxidant characteristics,[11] often allowing the sodium sulfite content to be reduced greatly or eliminated entirely.

In the formulation of photographic developers, there is a choice of developing agents so that a selection of a specific agent can be made to accomplish specific requirements. The existence of such a wide range of organic silver-complexing agents with a variety of inherent characteristics permits the photographic scientist for the first time to select the proper compound to accomplish a particular result. It is hoped that this freedom from the limited number of inorganic silver-complexing compounds will result in the perfection of monobaths of superior properties for more widespread usage.

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Mechanism of Development in Monobaths Containing Thiosulfate Ion

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Conflicting statements appear in the literature concerning the mechanism of development in monobaths. Experiments performed with monobaths containing thiosulfate as the fixing agent, using both motion-picture positive and high-speed negative films, indicate that such monobaths tend to produce considerably more silver than corresponding nonfixing developers when compared at equal optical densities. This appears to be the result of physical development of silver dissolved from unexposed grains upon adjacent exposed and partially developed grains. These results have significant effects upon the morphology of the silver developed and important implications for reversal processing.

In designing a photographic system suitable for rapid processing, the photographic chemist or engineer eventually is faced with certain difficulties which might be decreased if development and fixation could be combined into one treatment, by the use of a single solution, the so-called monobath. The most obvious advantage of a monobath is its simplicity, rather than the rapidity of processing attained, and one cannot look to monobaths for the utmost in processing speed. However, monobaths might also provide processing uniformity. Since the monobath does not require precise stopping action, and conventional development does, especially at high temperatures, the use of a monobath appears attractive as a means of making the process less critical with respect to mechanical configuration and precision. Although monobaths have interesting potentialities in this respect, they have not been generally accepted because of certain inherent shortcomings.

In 1959, Newman[1] published a comprehensive review of the progress made in formulating monobaths during the past seventy years, and from this review he reached several conclusions about the potential utility of monobaths, based upon the present knowledge of the mechanism of development in such formulations. Newman states that "even the best monobath will be the child of compromise," because the fixer will interfere with the normal process of development, and this will slow down development, leading to loss in emulsion speed, density, and contrast. According to Newman, these losses are due to "the ability of the fixer to dissolve out exposed silver halide from the emulsion before the light-struck particles have had a chance to develop." He mentions that the most severe silver halide losses occur in the areas of underexposure, corresponding to the toe of the characteristic curve. These conclusions are supported by Kendall,[2] who added thiosulfate to Kodak Developer D-19 and found that, with high-speed panchromatic films, the emulsion speed was reduced to only a small fraction of its normal level. Kendall also found an increase in contrast when relatively low concentrations of thiosulfate were added, but he did not offer an explanation for this effect. Kendall noted a reduction in graininess, although this was not surprising at the low emulsion speeds obtained.

Appearing shortly after Kendall's paper was a paper by Miller and Crabtree,[3] who demonstrated that the loss in speed and contrast may be overcome by increasing the alkalinity of the solution. These authors obtained approximately the same characteristic curve shape for a properly formulated developer-fixer as for a conventional developer, except for slightly higher fog level and lower speed. The authors did not think that these losses were severe enough to impair the photographic quality.

At the end of World War II, a paper became available as a result of the classified work done by Keller, Maetzig, and Möglich.[4] These investigators suggested the use of amphoteric metal salts as alkaline buffers for monobaths, and they formulated a monobath called "Glycal." They stated that this solution produced improved graininess and resolving power when compared with conventional developers, comparing favorably even with a "fine-grain developer." No explanation was given for these changes in microstructure, but, in 1953, Clarke, Milner, and Gomez-

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1. A. A. Newman, *Brit. J. Phot.*, **106**: 44, 66 (1959).
2. C. W. Kendall, *Am. Phot.*, **41**: 15 (1947).
3. H. A. Miller and J. I. Crabtree, *Am. Phot.*, **42**: 76 (1948).
4. I. M. Keller, K. Maetzig, and F. Möglich, "U. S. Dept. of Commerce P. B. 46,379," *Bibliography of Sci. and Ind. Repts., Office of Tech. Service, U. S. Dept. of Commerce*, **5**: 696 (1947). See also I. M. Keller, K. Maetzig, and F. Möglich, *Ann. Phys.*, **1** (6th series): 301 (1947).

Ibanez[5] demonstrated that, although it was possible to produce a monobath generating a density–exposure relationship similar to that of a conventional developer, the monobath developed much more silver, particularly in regions of low exposure. Since the increased amount of silver was not accompanied by an increase in density, the authors concluded that the monobath-developed grains were more compact than usual. In this connection, Murray and Spencer[6] also studied the effect of the addition of sodium thiosulfate to a developer, and they found three phases of development, suggesting that the mechanism of development may be rather unusual.

Consideration of the work of Keelan,[7,8] Merrill,[9] Levy,[10] Drumm,[11] and Levenson,[12] together with that of Miller and Crabtree, leads to the conclusion that monobaths may be designed to produce satisfactory sensitometric properties for certain restricted applications. Furthermore, the work of Kendall, Keller, and Clarke suggests that monobaths might produce less graininess and higher resolving power than conventional developers.

Consideration of the work of Clarke and co-workers leads to a conclusion very different from that reached by Newman. Newman concluded that the usual speed depression was due to "loss of light-struck halide" in monobath processing, and indeed this assumption appears to have been quite general among those working towards the formulation of monobaths. This assumption implies that there is a competition for the silver halide between the developing and the fixing components. However, Clarke and co-workers did not observe any loss of silver with a thiosulfate-containing monobath, but rather a substantial gain in the amount of silver developed, although the silver had low covering power. If Clarke's results are valid and general, then Newman's conclusion may lead to an erroneous assumption of the mechanism of development in monobaths. Clarke's results imply that physical development may play a major role in development by certain monobaths.

In studying the effect of silver halide solvents in a developer upon the microstructure of the developed image, Loveland[13] concluded that, for low-iodide emulsions, the main part of development appeared to be an intensification action in which silver was deposited by physical development upon grains which had already developed. James and Vanselow[14] studied the rate of solution of silver halide grains in solvent-containing developers, and they concluded that when an active developer contains a rapid-acting solvent, such as thiosulfate, "silver from a grain, which does not contain latent-image nuclei, may physically develop onto the silver of an adjacent developed grain and cause a significant increase in the amount of silver in the developed grain." These authors found that the addition of a low concentration of thiosulfate brought about a decrease in density, even though there was an increase in the amount of silver developed in the toe region.

Recently, Eggenschwiller and Jaenicke[15] have used model experiments to study the possibility of the occurrence of physical development in monobaths in which the solvent is thiosulfate. These authors conclude that the silver halide only, and not the silver–thiosulfate complex, is reduced in a monobath, and that physical development may be disregarded. Because it is difficult to explain the mechanism of the diffusion-transfer system on this basis, Eggenschwiller and Jaenicke conclude that the catalytic action of physical-development nuclei depends upon the size of the nuclei particles. They believe that the larger particles resulting from monobath development are less active than the colloidal particles used in diffusion-transfer physical development.

Still more recently, Klein[16] has studied the role of low concentrations of thiocyanate in reversal development and concluded that the sensitometric response may be predicted by assuming that the thiocyanate promotes physical development of silver from undeveloped grains onto chemically developed grains.

There is some disagreement, therefore, concerning the effect of the presence of thiosulfate in developers and in monobaths. Since the apparent potentialities of monobath processing are conditioned by a knowledge of the mechanism of monobaths, experiments have been carried out in these Laboratories to shed further light upon the role of physical development in monobaths containing thiosulfate ion.

Experimental

It seemed appropriate to repeat the work of Clarke, Milner, and Gomez-Ibanez,[5] and to ascertain why they found the monobath to produce more developed silver. Since the most obvious difference is in the presence of thiosulfate, it was decided to determine the effect of adding sodium thiosulfate to an active developer. The following developer was formulated, to be used with Kodak Fine Grain Positive Film:

Water	500 ml
4,4-Dimethyl-1-phenyl-3-pyrazolidone	2.0 grams
Hydroquinone	60.0 grams
Sodium sulfite (anhydrous)	65.0 grams
Potassium hydroxide	50.0 grams
Water to make	1.0 liter

pH adjusted to 12.0

To this developer, sodium thiosulfate was added in

5. R. G. Clarke, C. E. Milner, Jr., and J. Gomez-Ibanez, *Phot. Eng.*, **4**: 231 (1953).
6. H. D. Murray and D. A. Spencer, *Phot. J.*, **77**: 330 (1937).
7. H. S. Keelan, *J. Phot. Sci.*, **5**: 144 (1957).
8. ———, *Phot. Eng.*, **4**: 157 (1953).
9. W. Merrill, *Photography*, **34**: 60 (1954).
10. M. Levy, *Phot. Sci. & Eng.*, **2**: 136 (1958).
11. W. M. Drumm, *ibid.*, **1**: 147 (1958).
12. G. I. P. Levenson, *Functional Phot.*, **5**: 7, 32 (March 1954).
13. R. P. Loveland, in C. E. K. Mees, *The Theory of the Photographic Process*, rev. ed., Macmillan, New York, 1954, p. 511.
14. T. H. James and W. Vanselow, *Phot. Sci. & Tech.*, (2) **2**: 135 (1955).
15. H. Eggenschwiller and W. Jaenicke, *Phot. Korr.*, **95**: 149 (1959).
16. E. Klein, *J. Phot. Sci.*, **8**: 178 (1960).

various concentrations up to 32 grams/liter, and the resulting series of developers was used to develop sensitometric exposures for 10 sec at 100°F. Figure 1A displays the sensitometric curves for the control

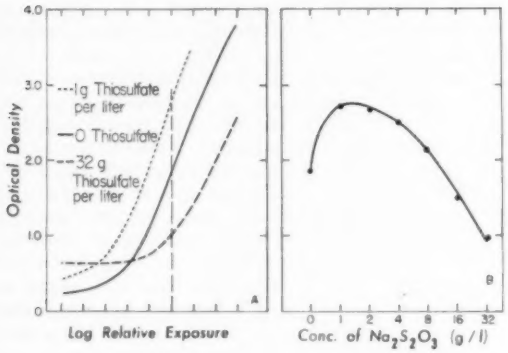

Fig. 1. Effect of thiosulfate upon sensitometric response (A) and upon developed density (B).

having no thiosulfate addition, and for two developers, one containing 1 gram, the other 32 grams of added thiosulfate. The addition of small amounts of thiosulfate to the developer caused an increase in density, whereas higher amounts caused a decrease in density, in keeping with the results obtained by Kendall. Figure 1B shows the variation of density at a constant exposure, as the thiosulfate concentration was varied over this range.

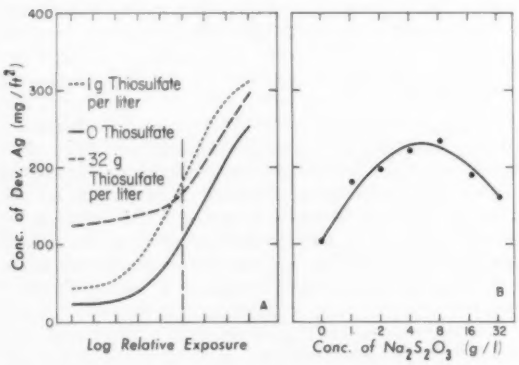

Fig. 2. Effect of thiosulfate upon the amount of silver reduced at various exposure levels (A) and at various thiosulfate concentrations (B).

The group of films thus tested was analyzed for developed silver at each density step. Plotting the amount of silver reduced, as a function of log exposure, resulted in the family of curves shown in Fig. 2A. From these results, it is apparent that the addition of up to 32 grams/liter of thiosulfate caused an increase in the amount of silver developed at each density. It may be seen in Fig. 2B that the amount of developed silver reached a maximum when about 8 grams of thiosulfate had been added, and then decreased with further addition, and this general relationship held for all exposure levels, except in the toe region. However, in no case was less silver developed as a result of the presence of the thiosulfate. Therefore, at high thiosulfate concentrations, the density bears no simple relationship to the amount of silver developed, as was also found by Clarke and co-workers. This suggests the importance of the "covering power" of the developed silver. Covering power may be defined as the optical density divided by the amount of silver developed in grams per square foot, and is thus a measure of the efficiency of the silver in producing opacity. If covering power is plotted as a function of thiosulfate concentration, the relationship shown in Fig. 3 is obtained for concentrations of 1 gram/liter and higher. From this graph it appears that covering power decreased exponentially with increasing thiosulfate concentration.

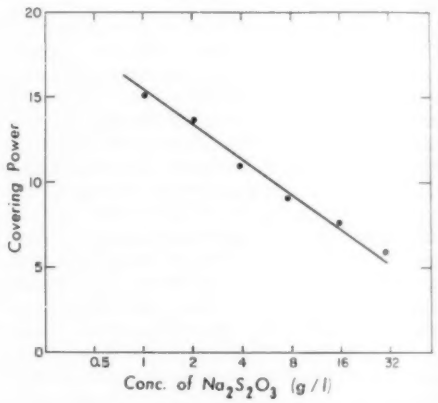

Fig. 3. Covering power as a function of thiosulfate concentration.

Since the solution used in these experiments did not contain any antifoggant, and since an antifoggant might be expected at least to alter the results, the experiments were then repeated with bromide and iodide added both separately and in conjunction with one another. The preliminary results indicated that, in this system, maximum antifoggant action was obtained when 16 grams of potassium bromide and 0.4 gram of potassium iodide were added per liter. Figure 4A shows the effect of adding 4 grams of thiosulfate per liter to a developer containing these concentrations of bromide and iodide, and the rather surprising increase in density is readily apparent. This increase is particularly interesting because the fog level was relatively unaffected. Figure 4B displays the same results in terms of the amount of silver developed, and it is seen that the effect of thiosulfate was to increase the amount of silver quite

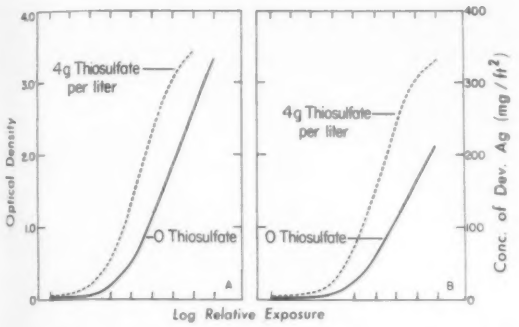

Fig. 4. Effect of thiosulfate upon sensitometric response (A) and upon amount of silver developed (B) in the presence of 16 grams of potassium bromide and 0.4 gram of potassium iodide per liter of developer.

markedly, at some densities by more than a factor of 2. Also, the amount of silver developed at fog level was not increased, and the thiosulfate may therefore be considered to have an image-amplifying effect.

When it was established that the addition of thiosulfate to a developer produced an increase in the amount of silver developed, it was recognized that these developers containing thiosulfate were very poor monobaths, because they did not accomplish fixing in reasonably short times. Hence, the formulas were modified somewhat in order to make useful solutions. Increasing the sodium thiosulfate concentration to 50 grams/liter, with general rebalancing of the formula, produced interesting results, and cleared the films in less than 10 min at 68°F.

The effect of thiosulfate in a working monobath was studied by comparing the solution with and without thiosulfate. Films were processed for various times in the developer, and the time selected was that which most closely matched in sensitometric response the

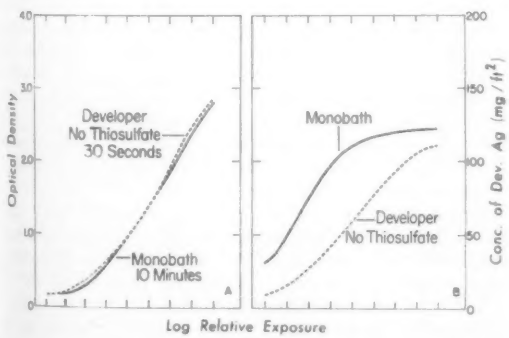

Fig. 5. Comparison of conventional developer and monobath with Kodak Fine Grain Positive Film, 5302.

results produced by the monobath. Figure 5A shows the sensitometric result produced by the developer after development for 30 sec, followed by fixation, compared with the result produced by the same developer, plus 50 grams of thiosulfate per liter, after processing to completion in 10 min. Although these sensitometric curves are well matched, analysis of silver, as plotted in Fig. 5B, indicates some very large differences. Processing in the monobath produced much more silver, but the same density as that which resulted from development in the absence of thiosulfate. In other words, the monobath process produced silver of considerably lower covering power. If covering power is plotted as a function of density for the monobath and the developer, the

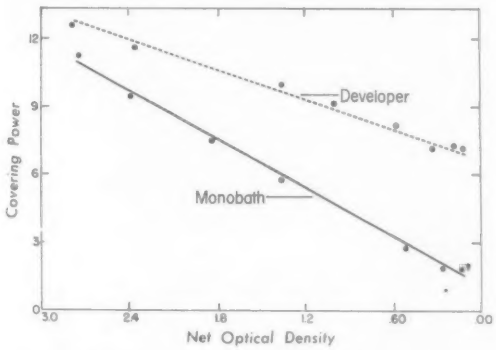

Fig. 6. Relationship between density and covering power for monobath and developer with Kodak Fine Grain Positive Film 5302.

relationship displayed in Fig. 6 is obtained. It is clear that the monobath produced lower covering power than the developer at every density, and it is also clear that covering power decreased as density decreased in either case. However, the covering power produced by the monobath falls off quite rapidly at the lower densities. At the minimum density, the monobath produced covering power only one-third as great as that produced by the developer.

All of the results thus far were obtained with Kodak Fine Grain Positive Film, but different results might be expected from a film of widely different characteristics, such as Kodak Tri-X Negative Film. However, it is evident from Fig. 7 that very similar results

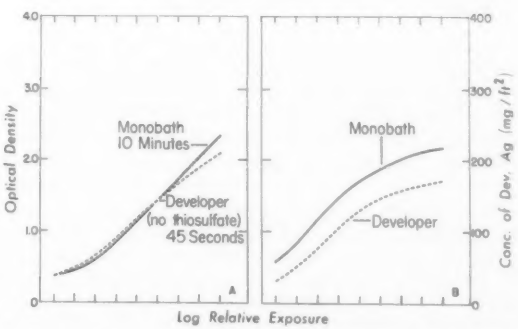

Fig. 7. Comparison of conventional developer and monobath with Kodak Tri-X Negative Film.

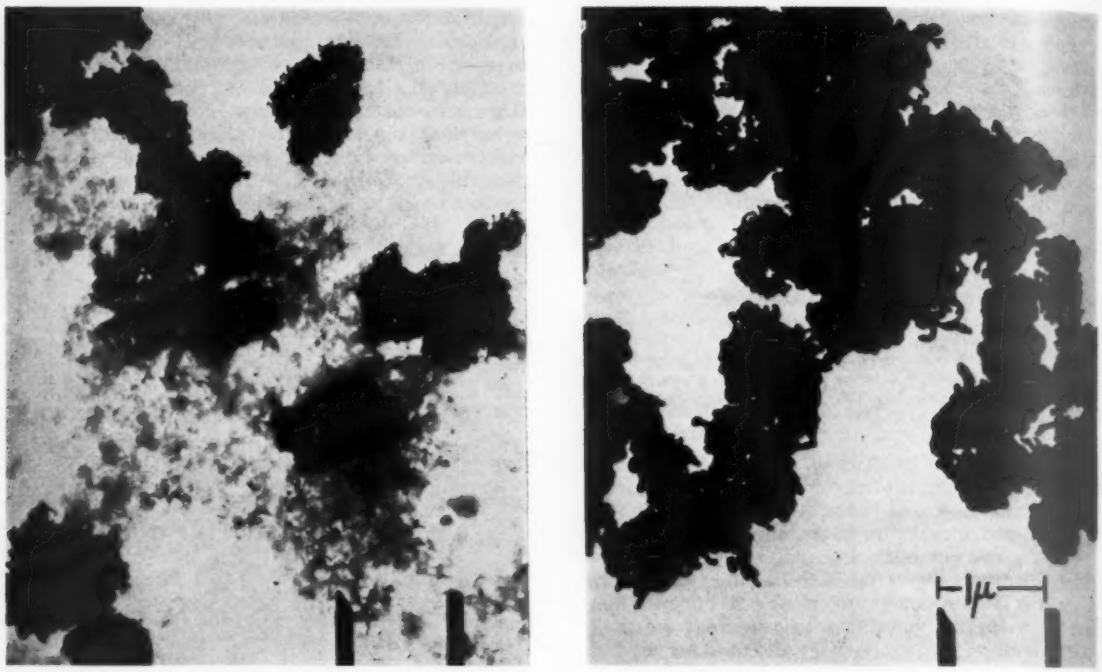

Fig. 8. Electron micrographs comparing silver developed in a developer and in a monobath at matched densities with Kodak Plus-X Negative Film. *Left*, developer; $D = 1.23$; Ag = 175 mg/sq ft. *Right*, monobath; $D = 1.27$; Ag = 365 mg/sq ft.

may be obtained with the coarser-grain film. Such results have been obtained with various types of film and monobath formulas, provided the monobath has thiosulfate as the fixing agent.

Since the increase in the amount of silver and the decrease in covering power would be expected to alter the size or morphology of the developed silver particles, electron micrographs were prepared. Figure 8 displays silver grains developed in the developer and in the monobath, and the increase in silver may be seen in the thickening of filaments in the fibrous structure.

Discussion

All the results obtained indicate that monobaths prepared with thiosulfate generally produce more developed silver than corresponding development in the absence of thiosulfate. The silver developed by such monobaths has low covering power, particularly at lower densities, and the covering power decreases exponentially with increasing thiosulfate concentration. This is in agreement with the results obtained by Clarke, Milner, and Gomez-Ibanez. Thus, the observed losses in density, speed, and contrast noted by Kendall, Newman, Miller, and others are not the result of corresponding losses in developed silver, but the result of decreased covering power occurring because of the presence of thiosulfate.

Since the action of thiosulfate is to increase the amount of silver but not the density, it seems probable that the size of the developed grains may not be increased, although the mass of the grains may be increased several-fold. An exp anation may be obtained from the electron micrographs, in which it may be seen that the effect of thiosulfate is primarily to thicken the dendrites making up the fibrous grain structure. Thus, considerable silver may be introduced into the grain without any increase in the density. This observation is in agreement with Loveland's results and the conclusion that may be drawn is identical with that of James and Vanselow: Silver from a grain which does not contain latent-image nuclei may physically develop onto the silver of an adjacent developed grain and cause an increase in the amount of silver developed.

Eggenschwiller and Jaenicke concluded that the silver–thiosulfate complex would not be reduced under these conditions, and that physical development should not occur. However, there seem to be only two reasonable sources for the additional silver developed. Either more grains are developed as a result of the thiosulfate, or more silver is being developed as a result of physical development. It is true that the solvent would bring about the development of grains having only internal latent-image or fog centers, whereas normal development might not. However, such development of additional grains would result in higher density without decreased covering power and, although this may be true at the

very low thiosulfate concentrations where an increase in density was observed, it does not seem a likely explanation for the large increases in silver observed at relatively high thiosulfate concentrations. Since physical development upon certain nucleating centers in separate receiving layers has been used in a variety of image-forming systems, it is not unlikely, then, that similar diffusion transfer occurs within the emulsion layer, with developed grains serving as nuclei for the physical development of silver from adjacent unexposed grains.

These conclusions have important implications with respect to reversal processes in which the unexposed silver halide is employed to form a positive image, as has been discussed by Klein. Klein developed films in developers containing low concentrations of thiocyanate, and then bleached the silver and redeveloped the residual silver halide, as is customary in the usual reversal process. He found that superimposition of the negative and positive images formed during this process did not result in a uniformly high density, but exhibited a definite minimum density in areas which had received low levels of exposure. This was true even though silver analysis did not show a corresponding minimum in the amount of silver developed. Miller[17] found similar results when the developer contained thiosulfate and he concluded that some of the unexposed silver halide was removed from the emulsion during development as a result of the solvent. This conclusion is supported in part by recent work of Eggenschwiller and Jaenicke[18] who believe that the degree of fixation is a function of the degree of exposure and development.

Results similar to those of Miller have been obtained by developing Kodak Fine Grain Positive Film in the following developer:

Water	500 ml
4,4-Dimethyl-1-phenyl-3-pyrazolidone	2.0 grams
Hydroquinone	60.0 grams
Sodium sulfite (anhydrous)	65.0 grams
Potassium hydroxide	50.0 grams
Potassium bromide	16.0 grams
Potassium iodide	0.8 gram
Sodium thiosulfate	108.0 grams
Water to make	1.0 liter

pH adjusted to 12.0

This developer differs only slightly from that used to determine the effect of thiosulfate in the presence of bromide and iodide.

The film was exposed, developed in this developer for 15 sec at 120°F, and then completely exposed to light; the residual silver halide was developed in the same solution.

Although this developer does not have exactly the same composition as that used by Miller, it is similar in that thiosulfate is present, and the resultant sensitometric response shown in Fig. 9 is quite similar to the response obtained by Miller. On the basis of Miller's explanation, one would expect to find considerably less silver developed at B than at C as a result of fixation of silver halide at B. Silver analysis of the developed strip indicated that the distribution of silver was as follows:

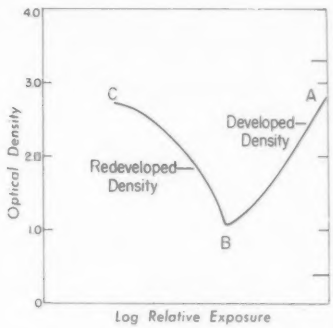

Fig. 9. Sensitometric response of a reversal process in which the developer contained thiosulfate. The amounts of silver developed were: at A, 374 mg/sq ft; at B, 341 mg/sq ft; at C, 281 mg/sq ft.

A — 374 mg of silver per square foot.
B — 341 mg of silver per square foot.
C — 281 mg of silver per square foot.

It is clear that the positive image is not a result of the development of corresponding silver because there is considerably less silver developed at C (the high density) than there is at B (the minimum density). One must explain why the amount of silver present at B does not impart corresponding density at least as high as at C. At B, some grains were exposed but a large proportion were not exposed. Upon immersion in the developer, the exposed grains began to develop, and the unexposed grains began to be dissolved and physically developed upon the exposed, developing grains. These unexposed grains impart little, if any, density, since the silver formed by physical development on the fibrous grains has very low covering power. On the other hand, at C, there were very few exposed grains but there were many unexposed grains. Since there was so much silver halide and so few sites for physical development in this area, all of the silver was not physically developed, but, rather, some of it remained as silver halide. This silver halide after re-exposure was developed chemically and thus had higher covering power.

In other words, the presence of thiosulfate in a developer, or a monobath, may cause the development of much more silver than would be expected on the basis of the density produced. It follows that there is then less silver halide remaining for redevelopment to a positive image than would be expected on the basis of the density of the negative image.

17. H. A. Miller, *PSA Jour.*, **14**: 103 (1948).
18. H. Eggenschwiller and W. Jaenicke, *Phot. Korr.*, **95**: 165 (1959).

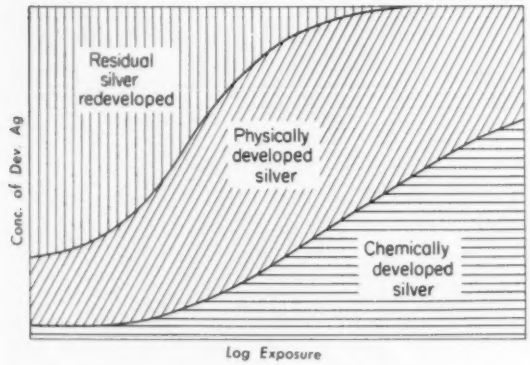

Fig. 10. Hypothetical representation of the distribution of silver in a reversal process where the developer contains thiosulfate.

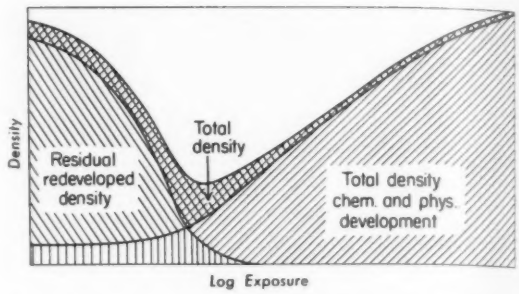

Fig. 11. Conversion of the silver distribution shown in Fig. 10 into a hypothetical sensitometric response, illustrating the minimum density resulting from the low covering power of the physically developed silver.

Figure 10 displays a hypothetical representation of the distribution of the silver present in a film when development is carried out in the presence of thiosulfate. Some silver is apparently chemically developed as a result of exposure, as shown by the lower right area. Some silver is also physically developed onto the chemically developed grains, and much of this silver was not affected by the original exposure. This is shown by the middle area of the graph. This leaves only the silver depicted in the upper left area available for redevelopment or diffusion from the emulsion during fixation. If this information is converted into density data, and if it is assumed that the physically developed portion of the silver has no density, a curve similar to that shown in Fig. 11 is obtained. The minimum density is clearly seen to be a result of the fact that the physically developed silver does not impart density comparable to that of chemically developed silver. The positive curve is not a mirror image of the negative curve for the same reason, as has also been discussed by Klein.

Conclusions

With regard to combined developer-fixers compounded with thiosulfate, the concept that the developer and fixer compete for exposed silver halide is not entirely correct. There is a related competition, but it is actually between two different types of development, since both chemical and physical development are involved, and there is in a sense competition between these means of development. More physical development relative to chemical development would be produced by increasing thiosulfate concentration, resulting in lower covering power, more compact silver structure, and a tendency towards the development of additional silver from surrounding grains. On the other hand, more chemical relative to physical development would produce higher covering power, because the fibrous structure of the chemically developed silver would tend to predominate over the more amorphic structure of physically developed silver.

Thus, the density, speed, contrast, covering power, and structure of developed silver depend upon the relative importance of chemical and physical development. Chemical development is first to commence, since in no case have the results appeared similar to those of postfixation physical development, although they tend to approach the type of result obtained by this procedure. Thus, it may be more accurate to say that the characteristics of the monobath are determined by the extent of chemical development that is allowed to occur prior to the primary activity of physical development.

With these conclusions in mind, the incorporation of developer and fixer in the same solution is not as impractical as it might at first seem. In fact, one could even consider the possibility of making a combined fixer-developer, in which fixation occurred first and then postfixation physical development produced the necessary density. It is true that one might expect results different from the usual, but not, necessarily, owing to unfavorable compromises. With films that are usually processed to their maximum contrast, such as x-ray films, one may expect monobaths to give lower contrast than normal because of the loss in covering power. Monobaths should be expected to increase fog level to a degree, as a result of the relatively large amount of silver physically developed, even though the covering power is low.

Since the morphology of the silver developed by monobaths appears to be markedly different from that developed in a more conventional manner, monobaths might be expected to produce interesting changes in image structure warranting additional study.

Acknowledgments

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A Photopolymerization Method of Preparing Three-Dimensional Terrain Models

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A photomechanical method, based on dye-sensitized photopolymerization, has been developed for the preparation of three-dimensional terrain models. The procedure involves the polymerization of an aqueous monomer solution by means of visible light. A contour map transparency, in which increasing height is represented by decreasing density, is projected into the photosensitive solution. The light initiates the polymerization of the monomer and converts it to an insoluble gelled polymer; the direct result is a three-dimensional terrain model. The height of the relief can be controlled by altering the exposure time or the light intensity. The freshly prepared polymer relief images are then used for making rubber molds, which serve for casting terrain models out of plaster or plastic. Three-dimensional terrain models up to a height of $\frac{3}{4}$ in. have been prepared.

Conventional methods for producing three-dimensional terrain models involve tracing, routing, clay modeling, or plaster carving, and involve much manual effort, long periods of time, and high costs. Recently, automated milling or routing machines have been employed for this purpose, but the equipment is complex and expensive, and the process is still time-consuming.

This paper presents a new and rapid photomechanical process, based on dye-sensitized photopolymerization, for preparing plastic three-dimensional master terrain models. Exposure of a photosensitive monomer solution through a variable-density contour transparency produces, in a matter of seconds, a solid polymer whose shape is controlled by the densities of the photograph. The resultant gelled polymer relief image can be readily molded in rubber, and from these rubber molds castings of plastic, plaster, or metal can be made.

Dye-Sensitized Photopolymerization

The three-dimensional map-making process consists of inducing polymerization of a mixture of monomers by exposing the mixture to visible light, which activates a dye present in the solution. The form of dye-sensitized photopolymerization utilized in this process was first reported in 1953 by Gerald Oster.[1] The sensitization mechanism differs from many types of photoactive catalysts in that visible light, rather than high-energy radiation, acts on a chemical system to produce free radicals capable of initiating polymerization.

The system involves a sensitizing photoreducible dye, a mild reducing agent (electron donor), and a vinyl monomer in an appropriate medium in the presence of ambient oxygen. These ingredients are dissolved in water, with polymeric materials added to adjust the viscosity.

The light-induced reaction can be represented as follows[2,3]:

(1) $\mathrm{Dye} \rightarrow \mathrm{Dye}^*$ (activated dye molecule)

(2) $\mathrm{Dye}^* + \mathrm{RH_2} \rightarrow \mathrm{DyeH_2} + \mathrm{R}$
(reducing agent) (leuco dye)

(3) $\mathrm{DyeH_2} + (\mathrm{O}) \rightarrow \cdot\mathrm{OH} + \cdot\mathrm{DyeH}$
(air) (free radical)

(4) $\cdot\mathrm{OH} + \mathrm{CH{=}CH_2} \rightarrow \mathrm{HO{-}CH{-}CH_2}\cdot$
(monomer)

(5) $\mathrm{HO{-}CH{-}CH_2}\cdot + n\,\mathrm{CH{=}CH_2} \rightarrow \mathrm{HO{-}[{-}CH{-}CH_2{-}]_{n+1}}$
(polymer)

The electron donor compound must be chosen so that it will not reduce the dye in the dark, but will reduce the light-excited dye molecules. Exposure to visible light containing wavelengths which the dye absorbs raises the dye molecules to a more energetic state (the triplet state) which permits the photoreduction of the dye to occur.[4] The reduction of the

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1. G. Oster, *Phot. Eng.*, **4**: 173 (1953).
2. ——, *Nature*, **173**: 300 (1954).
3. G. K. Oster, G. Oster, and G. Prati, *J. Am. Chem. Soc.*, **79**: 595 (1957).
4. A. H. Adelman and G. Oster, *ibid.*, **78**: 3977 (1956).

dye converts it to the leuco dye, a colorless form of the compound. The leuco dye is to some extent re-oxidized by oxygen. In this redox reaction, free radicals are produced which initiate the chain polymerization of the vinyl monomer. If a cross-linking agent such as a divinyl compound is also present, the resulting polymer will be an insoluble solid gel.

The polymerization proceeds in only the light-struck portions of the liquid mixture. These portions are converted into a solid gel structure. The depth to which the solution solidifies is determined by the intensity and length of the exposure to visible light. Therefore, if the light striking the solution is in an image pattern and of variable intensity, a polymer relief image is obtained. Unexposed solution containing unchanged monomer can be washed away with water, leaving the solidified three-dimensional image.

Preparation of 3-D Terrain Models

The preferred procedures for exposure of the monomer solution and processing of the polymer relief image are as follows:

Mixing the Monomer Solution

The final mixing of the ingredients is accomplished from stock solutions just prior to the exposure step. The sensitized solution contains the following major ingredients which are dissolved in water: (1) primary monomer, (2) cross-linking monomer, (3) sensitizing dye, (4) reducing agent, and (5) viscosity agent.

Exposure

The laboratory set-up for projection exposure is diagrammed in Fig. 1. Contact exposure has also been employed.

The photosensitive solution is placed in a container with a clear flat base, e.g., within a plastic cap on top of a glass plate. A variable-contrast contour transparency, prepared by the Dystrip Process,* is used for projection.

The solution is exposed through the clear base of the container by focusing the contour map image onto the top surface of the glass plate in contact with the solution. The focusing is achieved by means of a slide projector.

The exposure level in our work varied from 400 to 4000 ft-c at the focal plane, depending on the density of the photographic contour transparency. With the optimum formulation of the solution ingredients, an exposure time of 30–90 sec at 4000 ft-c yields a polymer image approximately $\frac{3}{4}$ in. high.

Processing

After exposure, the relief image is washed for 5–7 min in a tray of running cold water with manual agitation. This removes the unchanged monomer, leaving a fairly rigid cross-linked three-dimensional polymer terrain model.

Post-Hardening Treatment

Increased hardness and toughness of the photopolymer is sometimes desirable, e.g., when the relief-map image is to serve as a master form for molding. In this case, the photopolymer terrain model, immediately after the washing step, is covered with cold water (to absorb the heat of the exothermic reaction) and exposed to uniform illumination (4000 ft-c) for 5–7 min. This treatment causes further polymerization and hardening of the three-dimensional plastic model.

* These transparencies were kindly supplied by the U.S. Air Force Aeronautical Chart and Information Center, St. Louis, Mo.

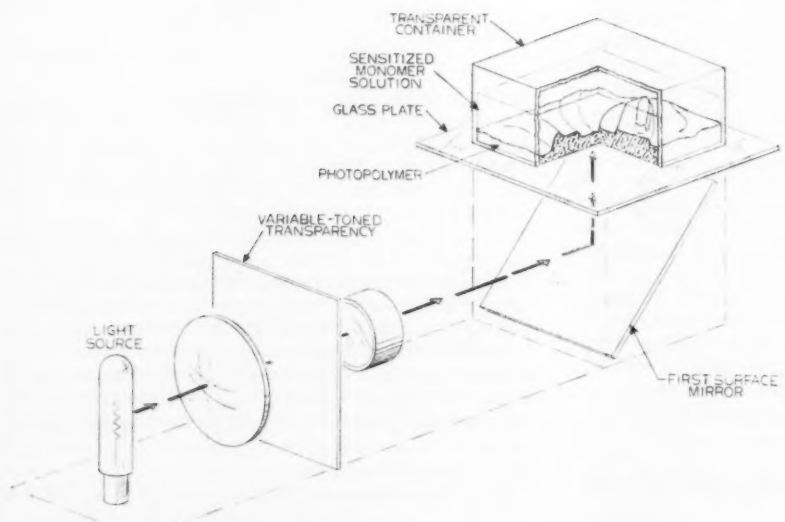

Fig. 1. Exposure of the photosensitive monomer solution.

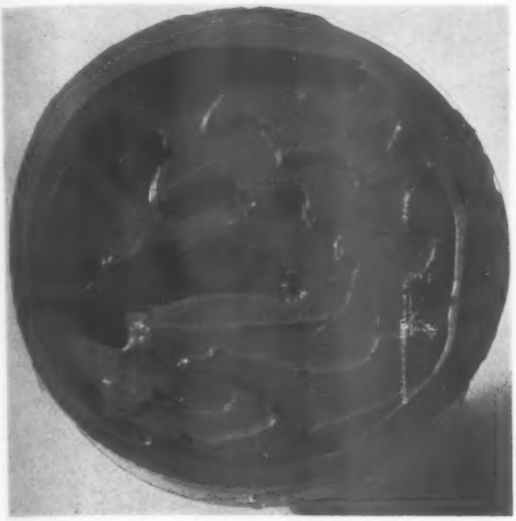

Fig. 2. Silicone negative mold of a "step" polymer relief image.

Molding and Casting a Permanent Model

The photopolymer relief image, prepared as described above, gives a faithful rendition in three dimensions of the contour densities and outlines in the original photograph. However, since it is actually a cross-linked gel structure containing occluded water, it does not possess dimensional stability on aging. Drying of the polymer causes a certain amount of shrinkage.

Therefore, to prepare a permanent three-dimensional terrain model by this technique, it is necessary to make a rubber mold from the photopolymer relief map shortly after the post-hardening step (Fig. 2). Silicone rubber (General Electric Grade No. RTV-20) has been successfully used for this purpose. The silicone sets up at room temperature, and no release agent is required with these photopolymer master models.

The silicone rubber mold serves as a negative, or intaglio, relief image of the contour terrain which can be stored to be used as needed for the casting of faithful bas-relief replicas of the original master terrain model. Plaster, plastic, and metal castings have been made successfully. Depending on the type of photograph used in the original exposure of the photosensitized monomer solution, either step or continuous-tone permanent castings of a three-dimensional contour map can be prepared.

Characteristics of Photopolymerization

Spectral Sensitivity

A large number of dyes will act to sensitize this polymerization system to visible light.[5] By proper choice of sensitizing dye, the three-dimensional imaging process can be made to respond to different portions of the spectrum. For example, a blue photo-reducible dye gives sensitivity to red light, a yellow dye to blue light, etc.

Tungsten lamps can be used in combination with conventional glass optics. Because the image can be formed by projection, optical reduction or enlargement of a contour map is possible.

Dye Bleach-Out Property

There are two general types of sensitizing dyes that work in this photopolymerization system: (1) dyes that recover their color rapidly by re-oxidation, even during exposure and (2) dyes that re-oxidize slowly and therefore do not fully regain their color until after exposure. For terrain model-making, the latter type of "slow recovery" bleaching dye is preferred. This bleach-out property confers two important advantages:

1. The growth of height of the three-dimensional terrain model can be observed during exposure, thus providing the operator with a visible guide to the progress of the reaction.
2. Since the light-absorbing medium is actually removed by bleaching during exposure, the active light can penetrate deeper into the solution as the polymerization proceeds, leading to production of greater polymer height than otherwise possible.

Height/Density and Height/Time Relationships

Conventional photographs cannot be used for this type of three-dimensional work because the highlights and shadows are not functions of height alone of the original subject. In order to attain image heights proportional to the original subject by means of photopolymerization, the densities of the photograph must be adjusted to the inherent properties of this photosensitive system.

The photographic speed of the current optimum formulations is adequate to yield $\frac{3}{4}$-in. polymer in 30–90 sec with 4000 ft-c illumination. The rate of height growth can be controlled by altering any of the following: (1) time of exposure, (2) intensity of light, (3) wavelength or color of the light, (4) concentration of the constituents of the photosensitive mixture.

In regard to control of polymer height by exposure conditions, it has been determined that the following general relationships characterize the photopolymerization of the monomer solution:

(1) At constant exposure time

$$\log (H/H_0) \propto D$$

(2) At constant density

$$H \propto t$$

where H_0 = height of polymer image at zero density of the projected images
H = height of polymer image
D = density of projected image
t = exposure time

5. G. Oster, U.S. Patent 2,850,445 (Sept. 2, 1958).

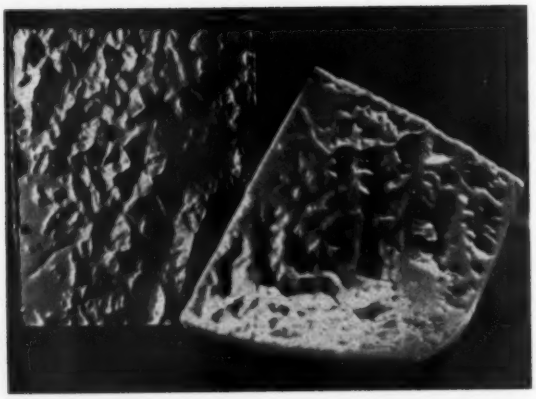

Fig. 3. Silicone rubber negative mold and subsequent positive plaster cast of a "continuous-tone" relief image (courtesy of the U.S. Air Force Aeronautical Chart and Information Center, St. Louis, Mo.).

Fig. 4. Photomechanically prepared terrain model using side lighting. (Courtesy of U.S. Air Force Aeronautical Chart and Information Center, St. Louis, Mo.)

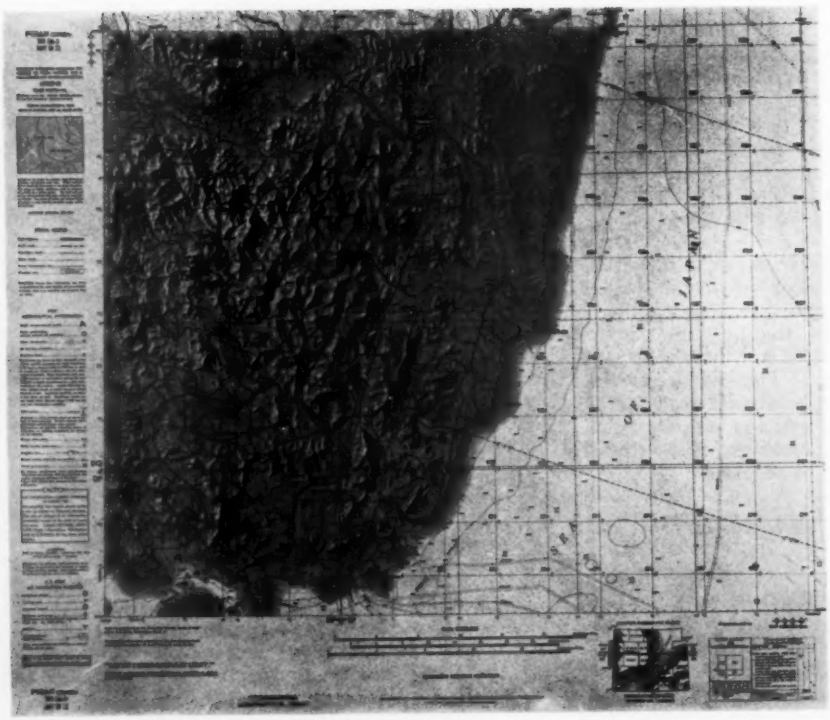

Fig. 5. Experimental two-dimensional shaded relief map. (Courtesy of U.S. Air Force Aeronautical Chart and Information Center, St. Louis, Mo.)

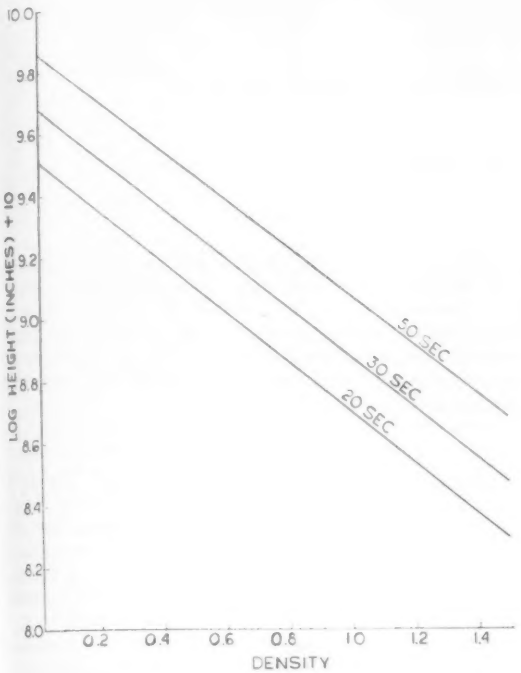

Fig. 6. Relationship between polymer height and density of the projected image, at constant exposure time.

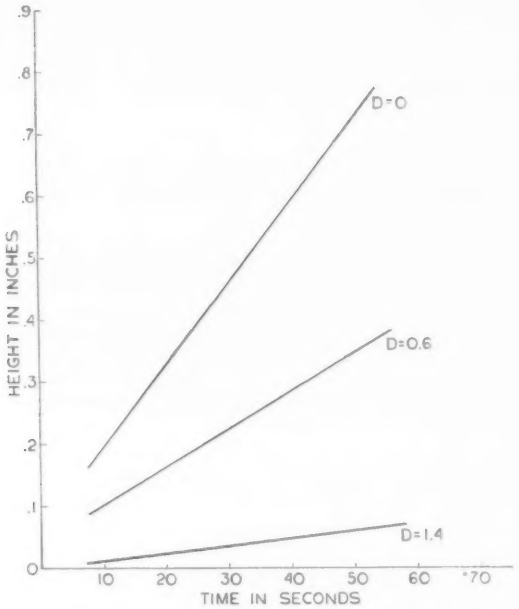

Fig. 7. Relationship between polymer height and exposure time for a given density of the projected image.

The actual curves of height vs. density and height vs. exposure time, based on measurements of a typical dye-sensitized photopolymerization system, are shown in Figs. 6 and 7. Using these curves as tools, polymer height can be made proportional to actual contour heights of a terrain. In one method, masks corresponding to contour outlines can be used in successive exposures, employing times regulated to give the height of polymer desired. However, our usual method is to employ a composite contour transparency (step or continuous), in which photographic density is adjusted so that D is proportional to log H at constant exposure. The composite contour transparencies we use were made by means of the Dystrip Process at the U.S. Air Force Aeronautical Chart and Information Center.

Either a bas-relief or an intaglio relief image can be obtained, depending on whether a positive or negative transparency is used for exposure.

Usefulness of the Photopolymerization Method

Work to date on polymer relief images has been limited mainly to qualitative studies, except for the investigation of the relation of height to certain variables in the system. Preliminary evaluation indicates that these photopolymer three-dimensional models possess sufficient accuracy to be employed as master models for molding and casting permanent relief maps suitable for many military and commercial uses. The U.S. Air Force Aeronautical Chart and Information Center has pioneered in the use of these photomodels in the preparation of shaded relief maps by controlled model photography (Figs. 3–5). By using proper side-lighting conditions, photographs showing shadowed terrain with a very realistic illusion of heights and depths can be obtained.

The process described here affords a rapid simple means of preparing permanent three-dimensional terrain models from properly adjusted photographic transparencies. Simple equipment and techniques are involved. Since the system is photographic in nature, the individual variations inherent in manual methods of making relief maps are eliminated.

Acknowledgment

Grateful acknowledgment is hereby made to the U.S. Air Force Aeronautical Chart and Information Center for their extensive cooperation in field testing the photosensitive solutions. In particular, thanks are due to Otto C. Stoessel, Jr., Chief, Richard Kahdeman, and Paul Willenbrink of the Printing Division, Aeronautical Chart and Information Center, for their efforts in adapting this process to the production of shaded relief maps. In addition, we would like to express our sincere appreciation to Dr. Gerald Oster, Polytechnic Institute of Brooklyn, for his valuable assistance as a consultant to this project.

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Some Properties of Silver Iodide Emulsions

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The sensitivity of pure silver iodide emulsions and of emulsions containing 1.3 mole % bromide is markedly increased by the presence of effective iodine acceptors. Several acceptors gave similar results at optimum concentrations. The emulsions in the absence of acceptor show a very high degree of low-intensity reciprocity failure which, however, is eliminated by the addition of the iodine acceptor. The emulsions in the absence of acceptor are more sensitive at −190°C than at room temperature, whereas the opposite is true in the presence of acceptor. The results are explained in terms of rehalogenation.

In a previous paper,[1] we showed that an alkaline pyrogallol developer used at elevated temperature was much more effective than the conventional high-energy Metol-hydroquinone or Amidol developers for use with silver iodide emulsions. We have used this pyrogallol developer in a study of some sensitometric properties of these emulsions. The iodide emulsions show some points of theoretical interest in that they exhibit extreme reciprocity failure in the low-intensity region, a failure which is largely eliminated by the addition of an iodine acceptor, and they exhibit greater sensitivity at −190°C than at room temperature.

Experimental Materials and Procedures

Two of the emulsions used were the same as described previously:[1] Emulsion A contained no halide other than iodide, and Emulsion B contained 1.3 mole % bromide. A third, D, was a coarser grained pure iodide emulsion with a relatively wide spread of grain sizes. The pyrogallol developer had the composition given previously and was used at 46°C for 40 min. Exposures through a step-wedge were made to tungsten light sources operated at 3000°K. The equipment used for the low-temperature exposures was copied after that described by Evans.[2] Liquid nitrogen was used as refrigerant to obtain a temperature of approximately −190°C.

Experimental Results

Previous workers have observed[1,3] that the speed of silver iodide emulsions can be markedly increased by bathing the emulsions, prior to exposure, in a solution of an iodine acceptor such as pyrogallol, sodium sulfite, sodium nitrite, or silver nitrate. Our results confirm these earlier observations. Figure 1 shows characteristic curves for Emulsion A for exposures made after treatments in various solutions. In the absence of treatment (Curve C), only a faint image was obtained upon development. A simple water wash for 5–60 min caused a significant increase in speed (W) and a 5-min treatment in sodium hydroxide solution produced a further increase in speed. The most effective agents, however, were pyrogallol, *p*-hydroxyphenylglycine (glycin), hydroquinone (curve not shown), silver nitrate, and sodium sulfite. The characteristic curves obtained for film samples bathed for 5 min in solutions of the various agents at optimum concentration, then dried before exposure, were nearly the same for all five agents. Sodium nitrite (N) was less effective.

The silver iodide emulsions show a high degree of low-intensity reciprocity failure, as illustrated in Fig.

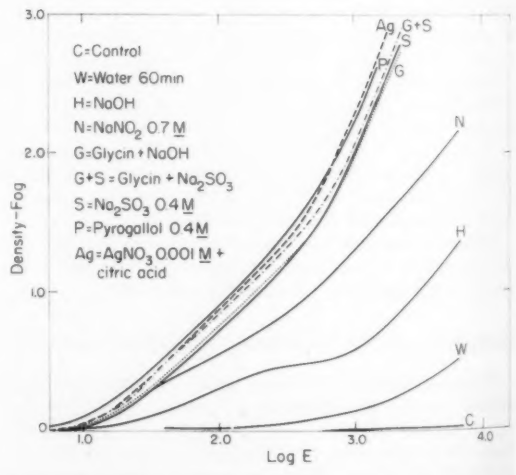

Fig. 1. Characteristic curves for Emulsion A, exposed 8 sec at room temperature to a 500-w lamp at 3000°K; effect of halogen acceptors.

Communication No. 2166 from the Kodak Research Laboratories. Received 12 April 1961.

1. T. H. James and W. Vanselow, *Phot. Sci & Eng.*, **5**: 21 (1961).
2. C. H. Evans, *J. Opt. Soc. Am.*, **32**: 214 (1942).
3. E. A. Sutherns, *J. Phot. Sci.*, **8**: 118 (1960).

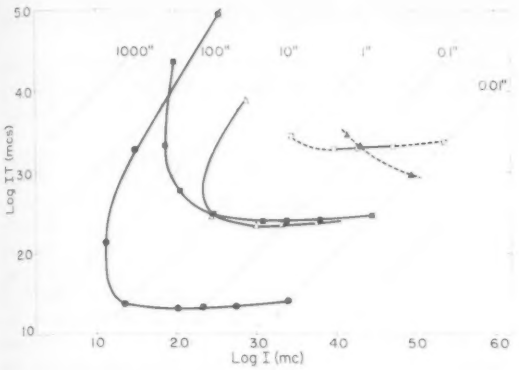

Fig. 2. Reciprocity-law-failure curves for Emulsions A and B, exposed at room temperatures: ▲A, sulfur sensitized, density 0.5; ●B, unsensitized, density 0.25; △B, unsensitized, density 0.5; □B, unsensitized, density 1.0; ■B, sulfur sensitized, density 1.0. All densities were corrected for fog.

2 for Emulsion A and for two samples of Emulsion B, one prepared without chemical sensitizing, the other given a sulfur-sensitizing treatment which would have produced a high degree of sulfur sensitization in a conventional silver bromide material. Both samples of Emulsion B show almost complete loss of sensitivity at sufficiently low exposure intensity; the loss occurs at a somewhat higher intensity for the unsensitized B than for the sensitized material. The pure iodide emulsion, A, exhibits the low-intensity failure at even higher intensities than B. Low-intensity failure is already marked in the region, 0.1–0.01 sec.

The presence of a good iodine acceptor during exposure largely eliminates reciprocity failure. Curves for both A and B are shown in Fig. 3.

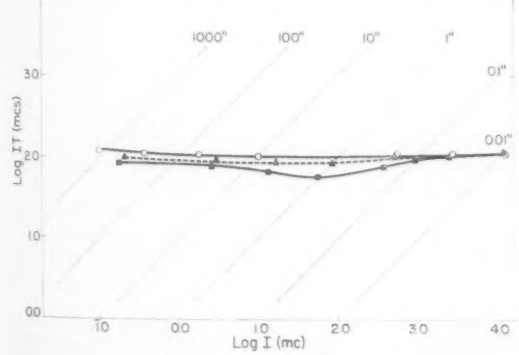

Fig. 3. Reciprocity-law-failure curves for Emulsions A and B exposed at room temperature after treatment for 5 min in sodium sulfite, 5 grams/liter at 20°C: ▲A, sulfur sensitized, density 0.5; ○B, unsensitized, density 0.8; ■B, sulfur sensitized, density 1.0.

The silver iodide emulsions without pretreatment are much more sensitive at −190°C than at room

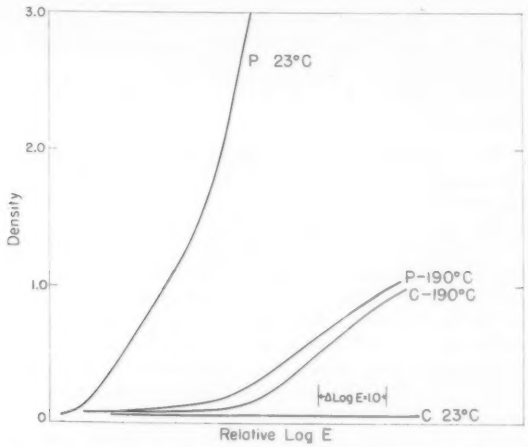

Fig. 4. Comparison of exposures at room temperature and at −190°C; Emulsion A exposed 600 sec to a 500-w lamp at 80 cm. Curves marked "P" apply to emulsion pretreated in pyrogallol solution, 5 grams/liter for 5 min.

temperature (Fig. 4). The pyrogallol-treated emulsions, on the other hand, are considerably less sensitive at the low temperature, a result more consistent with the behavior of silver bromide materials.

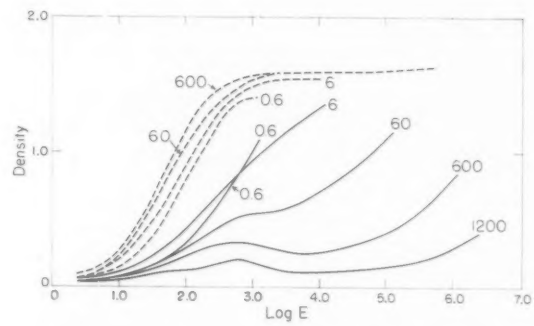

Fig. 5. Characteristic curves for Emulsion D exposed at room temperature or at −190°C. The numbers on the curves refer to exposure times in seconds. Solid curves, room temperature; broken curves, −190°C.

Figure 5 shows the characteristic curves obtained with the coarser-grained silver iodide emulsion, D, exposed for various times. The solid curves represent exposures made at room temperature and illustrate the pronounced low-intensity failure of this material. The broken curves represent exposures made at approximately −190°C. The relatively small reciprocity failure at this temperature is of the high-intensity type.[4] For all intensities, the sensi-

4. M. Biltz (*J. Opt. Soc. Am.*, **42**: 898 (1952)) and G. C. Farnell (*ibid.*, **47**: 843 (1957)) have observed a similar high-intensity failure for some silver iodobromide emulsions.

tivity of the material is greater at the low temperature, but the difference becomes smaller the higher the intensity.

Discussion

The untreated silver iodide emulsions show an unusually large degree of low-intensity reciprocity failure, whereas the emulsions treated with a good iodine acceptor before exposure show little or none. The effect of the iodine acceptor suggests that the low-intensity failure of the iodide emulsions is caused by rehalogenation.[5] A rehalogenation could occur either by diffusion of the positive holes to the latent-preimage or -subimage silver centers, followed by reaction to form silver ions and iodide ions, or by a combination of the holes with electrons originating in the thermal decomposition[6] of latent-preimage specks. The photographic result of either process would be the same, i.e., a loss of effective latent image. A good iodine acceptor, by reacting with the positive holes, could prevent the rehalogenation and thus increase the effective photographic speed.

The greater efficiency of the higher-intensity exposures of the untreated emulsions can be explained in terms of the more rapid growth of the latent-preimage and -subimage specks into full latent-image nuclei. Such nuclei should be far less susceptible to thermal decomposition,[6] and may be less susceptible to attack by positive holes.[7] In addition, the high-intensity exposures may favor combination of the holes to form iodine molecules, which may be less effective than the holes in causing rehalogenation of the silver.

Sutherns[3] points out that his experimental results show a lack of correlation between the effect of halogen acceptors on the photographic speed and the print-out speed of his silver iodide emulsion. He suggests, as a possible alternative to the halogen-acceptance mechanism, that the increase in photographic speed might be explained in terms of a photosensitive complex formed with silver ions at the grain surface. The amounts of photolytic iodine formed in normal latent-image exposures, however, differ by orders of magnitude from the amounts formed in print-out exposures, and the lack of correlation observed by Sutherns may not be a pertinent argument against the importance of halogen acceptance in the increased photographic speed. It appears that our results can be explained more easily in terms of halogen acceptance, since the various iodine acceptors, including silver ion or silver citrate, all produce nearly the same photographic effect when used at optimum efficiency.

The silver iodide emulsions show the unusual behavior of being more sensitive at $-190°C$ than at room temperature in the absence of added iodine acceptor. This greater sensitivity at the low temperature can be attributed to a smaller degree of rehalogenation. The positive holes probably are immobile at the low temperature, whereas the photoelectrons can move through the conductance band until trapped. As the emulsion warms up, following the exposure, electrons are liberated from shallow traps and latent-image silver is formed at more favorable trapping sites under conditions similar to those existing when a high-intensity exposure is made at room temperature. The added iodine acceptor under these conditions exerts little influence upon sensitivity.

5. Cf. W. F. Berg, *Trans. Faraday Soc.*, **44:** 783 (1948).
6. Cf. J. H. Webb and C. H. Evans, *J. Opt. Soc. Am.*, **28:** 431 (1938); J. H. Webb, *ibid.*, **40:** 3, 197 (1950).
7. J. W. Mitchell, *J. Phot. Sci.*, **6:** 57 (1958).

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Effect of Temperature of Exposure on Photographic Sensitivity and Development Rate

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The effect of the temperature and intensity of exposure upon the rate of development of a silver iodobromide emulsion was determined for exposures of 0.0005-sec and 1-min duration made at 23°, −178°, −186°, and −196°C. The rate of development of the 1-min exposure increased with increasing temperature in the −178° to −196° range, whereas the rate of development of an equivalent 0.0005-sec exposure was nearly independent of temperature over this range. The rates of development of the low-temperature exposure areas were all much smaller than the rates of development of room-temperature exposure areas.

The latent image formed at −196°C appears to be highly disperse and to consist of very small centers. The fact that the rate of development of latent image formed by the 1-min exposure increased with increasing temperature of exposure over the range, −196° to −178°, implies that exposure at the higher temperature results in the formation of larger latent-image centers. This suggests that latent-image silver actually is formed at temperatures only slightly above −196°C during the 1-min exposure period.

Published data on exposures of photographic materials to light at temperatures of liquid air (−186°C) and liquid nitrogen (−196°C) indicate that the sensitivity of most materials which have not been spectrally sensitized is roughly an order of magnitude lower at these temperatures than at normal room temperatures.[1–3] The difference in sensitivity is sometimes even smaller than this, however, and M. Debeauvais-Wack[4,5] found that an Ilford G-5 nuclear-track emulsion exposed to moderate-intensity light is actually more sensitive at the low temperature than at room temperature, although it is less sensitive for a high-intensity exposure. We have observed that pure silver iodide emulsions exposed in the absence of halogen acceptor are more sensitive at about −190°C over a wide range of light intensities than at 23°C, although in the presence of halogen acceptor they are less sensitive at the low temperature.[6]

Most of the work described in the literature involved a single time of development in a particular developer. Biltz[7] and Farnell[2,3] showed that the quantitative results depended on the developer used, and Farnell gives some data for two times of development in Kodak Developer D-19b which show that the relative speed difference of some experimental iodobromide emulsions exposed at 20° and −196°C was smaller when the longer time of development was used, but the effect of the duration of development does not appear to have been systematically studied previously.

Many emulsions show no reciprocity-law failure at −196°C for conventional development. Biltz[7] observed a high-intensity failure at this temperature for surface development of certain experimental emulsions, and this observation was confirmed by Farnell.[3] The *D*-vs.-log-*E* curves for the high-intensity exposures showed much lower contrast than those for low-intensity exposures at this temperature. This high-intensity reciprocity failure has been attributed to recombination of photoelectrons and positive holes.[3] The development conditions used by Biltz and by Farnell (e.g., 3 min in the *p*-hydroxyphenylglycine–carbonate developer) are relatively mild, and results to be included in this paper suggest that the low contrast might be a consequence of a relatively low degree of development.

Farnell has made the interesting observation that the sensitivity at liquid-oxygen temperature (−183°

Communication No. 2189 from the Kodak Research Laboratories, presented at the Annual Conference, Binghamton, N.Y., 26 May 1961. Received 24 May 1961.

1. Cf. C. E. K. Mees, *The Theory of the Photographic Process*, rev. ed., Macmillan, New York, 1954, p. 232.
2. G. C. Farnell, *Phil. Mag.*, **43**: 289 (1952).
3. ———, *J. Opt. Soc. Am.*, **47**: 843 (1957).
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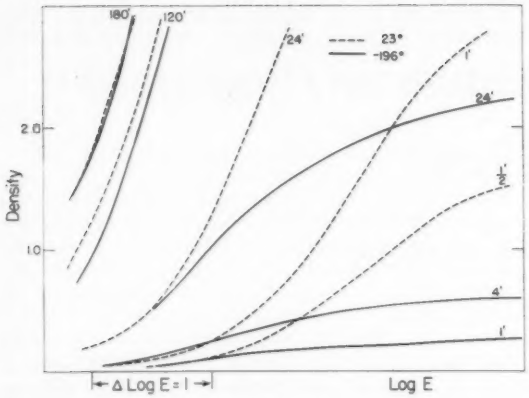

Fig. 1. Characteristic curves for a Strobonar exposure. Broken curves, 23°C at 95 cm; solid curves, −196°C at 30 cm. Metol–ascorbic acid development at 20°C for the times, in minutes, specified by the numbers on the curves.

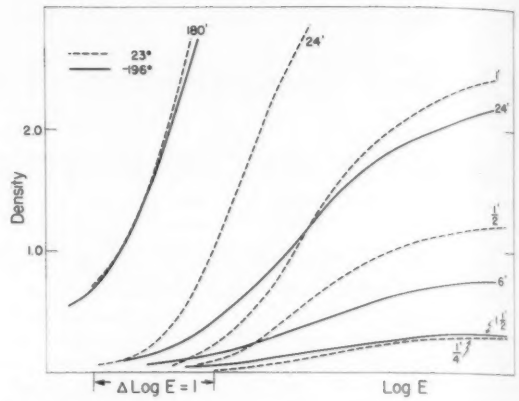

Fig. 2. Characteristic curves for a 1-min exposure. Broken curves, 23°C, 100-w, 80 cm; solid curves, −196°C, 500-w lamp, 80 cm. Lamps operated at 2650°K. Metol–ascorbic acid development at 20°C for the times specified on the curves.

C) is higher than that at liquid-nitrogen temperature (−196°C). Some of his data show a greater difference in sensitivity for low-intensity exposures than for high. Farnell made his exposures with the film immersed in the liquid nitrogen and oxygen, and it might be feared that some chemical action of oxygen would influence the results. However, our tests in which we used the highly inert liquid argon (−186°C) tend to confirm Farnell's results. Moreover, we obtained substantially the same results, both with liquid nitrogen and liquid argon, whether the film was immersed in the liquid or was pressed tightly against a thin aluminum cylinder filled with the liquid and surrounded by a Thermos flask. Our results do suggest, however, that the increased speed which Farnell observed at liquid-oxygen temperatures, relative to liquid-nitrogen temperatures, might only occur for incomplete development. We observed a higher *rate* of development by both D-19 and the Metol–ascorbic acid surface developer for moderate-intensity exposures made at liquid-argon temperature than for exposures made at liquid-nitrogen temperature, although the characteristic curves for the exposures made at the two temperatures coincided when development was prolonged.

Experimental Procedure

For the exposures at low temperatures, the film was placed lengthwise along the outside of a thin aluminum tube, 2 in. in diameter and 18 in. long, sealed at the bottom. The film was held against the tube by a sheet of heavy Kodapak, 5½ in. by 13 in., wrapped tightly around the film and tube and secured to it by double wrappings of string at several places along the length of the tube. A felt collar wrapped around the top of the tube was thick enough to make the tube fit snugly in the top of a Dewar tube 2⅜ in. in internal diameter. After the film was secured in place, the aluminum tube was placed in the Dewar tube and filled with the refrigerant liquid. About 1 min was allowed for temperature equilibrium before exposure. Tests showed that longer times allowed for equilibration did not change the photographic results, and measurements made by Evans[8] indicate that equilibrium should be reached within 30 sec. The refrigerants used were liquid nitrogen, liquid argon, and a mixture of about equal parts nitrogen and argon (measured temp., −191°C).

Exposures were made to tungsten lamps operated at 2650°K at a distance of 80 cm and to a Strobonar I flashlamp operated at a distance of 30 cm or 95 cm. The flash duration of the Strobonar is approximately 0.5 msec and the light output is rated as approximately 80 lumen-sec/sq ft at a distance of 4 ft from the lamp. The candlepower rating of the 500-w lamp is 314 and that of the 100-w lamp 73.2 at 2650°K.

The photographic material was Eastman Fine Grain Release Positive Film, Type 5302. Sensitometric exposures were made by placing a step wedge (0–4 density range) in contact with the film beneath the Kodapak wrapping on the aluminum tube. Tests also were made, either with or without a step wedge, in which the film was attached to a flat aluminum holder which was then immersed directly in the liquid nitrogen or argon contained in a Dewar tube. Exposures in all cases were made through the clear glass of the Dewar tube.

Some sensitometric exposures also were made on film held against a flat face recessed in a thick aluminum cylinder in an apparatus which essentially duplicates that described by Evans.[8] The temperature, as measured by a thermocouple, varied by about 10° from top to bottom of this tube, and substantial variations were observed in the developed density from top to bottom on 10-in. strips of film exposed without a step wedge in this apparatus. This equipment was used to obtain the data for an exposure temperature of approximately −178°C. The accuracy of the temperature control for these data is much inferior to that obtained with the thin aluminum cylinder filled with liquid nitrogen on liquid argon.

The developers used were the conventional D-19 and the Metol–ascorbic acid M-AA-1 surface developer of pH 9.8. Development was carried out in the nitrogen-atmosphere equipment with nitrogen-burst agitation.

8. C. H. Evans, *J. Opt. Soc. Am.*, **32:** 214 (1942).

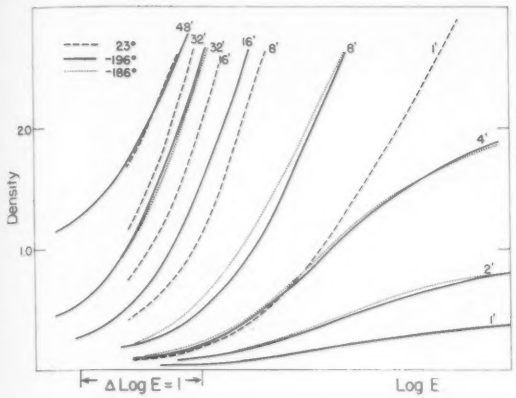

Fig. 3. Characteristic curves for a Strobonar exposure. Broken curves, 23°C; dotted curves, −186°C; solid curves, −196°C.; all at 95 cm. The curves for the two low-temperature exposures have been shifted 0.6 unit along the log *E* axis. D-19 development at 20°C.

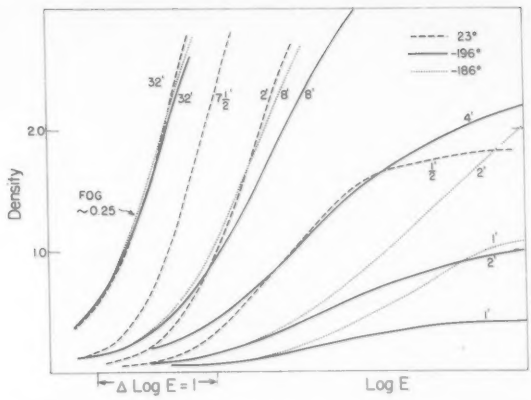

Fig. 4. Characteristic curves for a 1-min exposure. Broken curves, 23°C, 100-w lamp; dotted curves, −186°C, 500-w lamp; solid curves, −196°C, 500-w lamp. D-19 development at 20°C. The curves for the two low-temperature exposures have been shifted 0.63 unit along the log *E* axis.

Experimental Results

Tests made with the thin aluminum cylinder filled with nitrogen or argon showed that uniform densities are obtained over the entire 10-in. length of the exposure area, and were substantially the same as those obtained by equivalent exposure of the film held against an aluminum sheet and immersed in the liquid nitrogen or argon. The curvature of the film held against the aluminum cylinder caused some variation in density across the width of the exposed strip, but this variation was of minor importance when the film strip was carefully aligned along the vertical axis of the tube. The possibility that localized heating might result from the long exposure (1 min) to the 100- and 500-w lamps was discounted by tests which failed to show any effect of the introduction of a water cell or a Pittsburgh Plate Glass No. 2043, 2-mm-thick infrared filter into the light path.

The initial rate of development of latent image formed by a moderate- or high-level exposure at −196°C is much lower than that of latent image formed at room temperature. This is illustrated for the Metol–ascorbic acid surface developer by the characteristic curves plotted in Figs. 1 and 2, and for D-19 by the curves plotted in Figs. 3 and 4. In Fig. 1, curves for the Strobonar exposure at 95 cm at room temperature are compared with those for exposure at 30 cm at −196°C. The curves for the low-temperature exposure have been shifted along the log *E* axis so that the 180-min development curve coincides with the corresponding curve for exposure made at room temperature. In Fig. 2, curves for a 1-min exposure to the 100-w lamp at room temperature are compared with those for a 1-min exposure to the 500-w lamp at −196°C, again with adjustment along the log *E* axis to produce coincidence of the 180-min development curves for the two exposure temperatures.

In Fig. 3, results for D-19 development are given for the Strobonar exposures made at a lamp distance of 95 cm at room temperature, −186°C, and −196°C. The log *E* positioning of the curves has been adjusted to obtain coincidence of the curves for 48-min development. A log *E* shift of 0.6 was required for both the −186° and −196°C exposures to obtain coincidence of the curves with the room-temperature curve. Hence, the photographic speed for both low temperatures was one fourth that for room temperature for the prolonged development. The curves for the −186° and −196°C exposures substantially coincided at all development temperatures for the Strobonar exposure, but the rates of development for the two low-temperature exposures were much lower than that for the room-temperature exposure.

In Fig. 4, results are given for a 1-min exposure at each of the three temperatures. The curves for −186° and −196°C have been shifted 0.63 log *E* unit to make the curves for 32 minutes' development coincide. Hence, the photographic speed at the low temperatures was 0.23 that at room temperature. The speed at −186°C was substantially the same as that at −196°C. However, comparison of the curves for short times of development shows that, contrary to the results obtained with the Strobonar exposures, the rate of development of the latent image produced by the 1-min exposure at −186°C is nearly double that of the latent image produced at −196°C.

A comparison of characteristic curves obtained by Strobonar and 1-min exposures made at liquid-nitrogen temperatures indicates that the rate of development in D-19 of latent image formed by the 1-min exposure is nearly the same as, although possibly slightly faster than, that of latent image formed by the 0.5-msec exposure. For exposures at liquid-

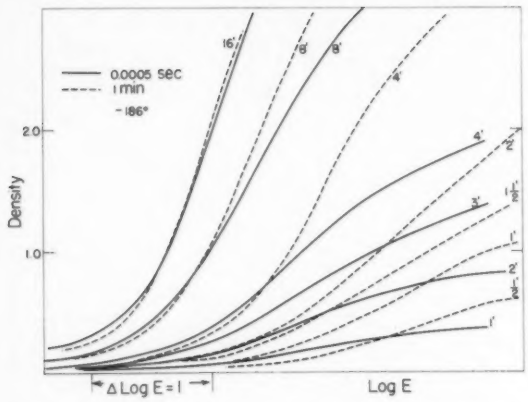

Fig. 5. Comparison of 0.5-msec and 1-min exposures made at −186°C. Solid curves, Strobonar, 95 cm; broken curves, 500-w lamp, 80 cm. D-19 development at 20°C.

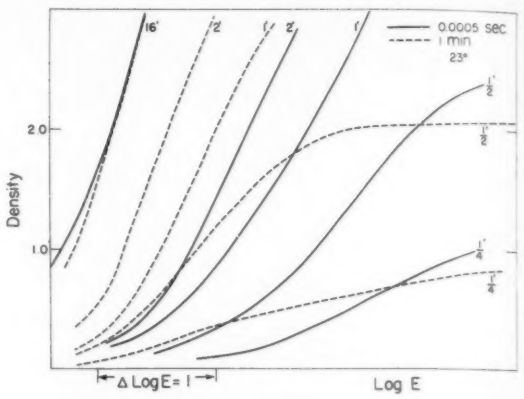

Fig. 7. Comparison of 0.5-msec and 1-min exposures made at 23°C. Solid curves, Strobonar, 95 cm; broken curves, 500-w lamp, 80 cm. D-19 development at 20°C.

argon temperature (Fig. 5), the rate of development of the latent image produced by the 1-min exposure is clearly greater, and at the highest exposure levels is more than twice that produced by the 0.5-msec exposure. For exposures at −178°C, the relative rate of development of the 1-min exposure area is greater still (Fig. 6). In Figs. 5 and 6, a log E adjustment has been made to produce near coincidence of the 1-min and 0.5-msec curves for 16 minutes' development. A comparison of the two exposures made at room temperature is shown in Fig. 7.

Results obtained with the Metol–ascorbic acid surface developer were similar to those obtained with D-19. Figure 8 shows a comparison of the rates of development of latent image formed by equivalent high-level exposures made for 1 min and for 0.5 msec at −186° and −196°C. The film in these tests was immersed directly in the refrigerant. The exposures correspond to the maximum obtained with the Strobonar lamp at 95 cm from the film with no filter or neutral density in the light beam. The 1-min exposure level was chosen so that the characteristic curves obtained with the Strobonar and 1-min exposures coincided for 180 minutes' development. The rates of development of the latent images formed by the two exposures at −196°C are substantially equal, but the image formed by the 1-min exposure

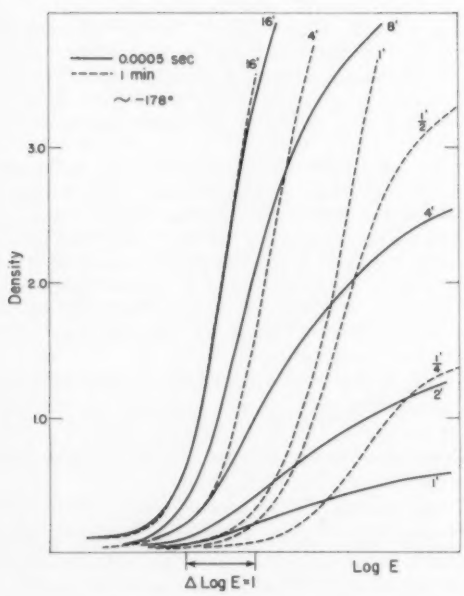

Fig. 6. Comparison of 0.5-msec and 1-min exposures made at −178°C. Solid curves, Strobonar, 95 cm; broken curves, 500-w lamp, 80 cm. D-19 development at 20°C.

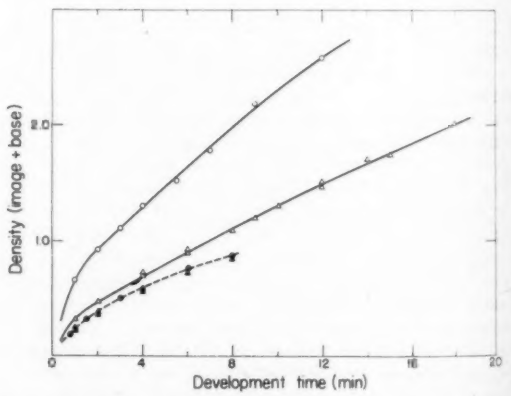

Fig. 8. Density–time of development curves for exposures made while film was immersed in liquid nitrogen or argon. ○, 1 min, −186°C; △ 0.5 msec, −186°C; ●, 1 min, −196°C; ▲ 0.5 msec, −196°C. Metol–ascorbic acid development at 20°C.

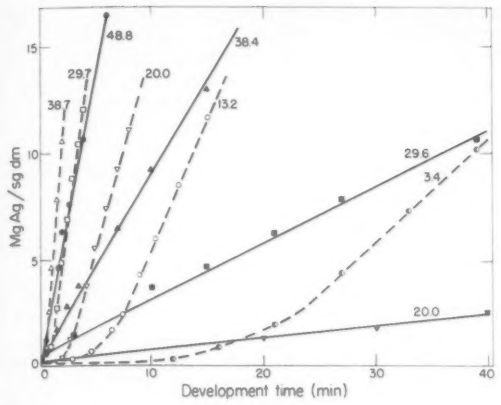

Fig. 9. Effect of temperature of development upon the rate of development of latent image formed at 23°C (broken curves) and −196°C (solid curves). Metol–ascorbic acid developer, pH 8.5. The numbers on the curves refer to temperature in °C.

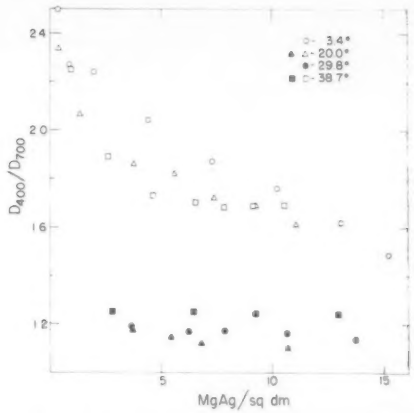

Fig. 10. Effect of temperature of development on the ratio of densities measured at 400 mμ and 700 mμ for exposures at 23°C (open points) and at −196°C (solid points).

at −186°C developed about twice as fast as that formed by the 0.5-msec exposure at that temperature.

Results obtained with D-19 development of film exposed while it was immersed in the refrigerant showed that the rate of development of latent image formed by the 1-min exposure increased with increasing exposure temperature (−196°, −191°, −186°C), whereas the rate was substantially the same for latent image formed by the 0.5-msec exposure at −196° and −186°C.

The temperature-dependence of development of a latent image formed at −196°C is considerably greater than that of an equivalent image formed by a high-level exposure at room temperature. Figure 9 shows development-time curves for a 1-min exposure to the 500-w lamp at −196°C and for a 1-min exposure to the 100-w lamp at 23°C. Silver per square decimeter is plotted against the time of development. The activation energies, calculated from the slopes of the straight-line portions of the curves, are 13.7 kcal/mole for the 23°C exposures and 23.7 kcal/mole for the −196°C exposures. Similar results were obtained for development of latent image formed by a 0.5-msec exposure. The developer had the composition: Metol, 1.4 grams; ascorbic acid, 3.3 grams; potassium bromide, 1.0 gram; sodium metaborate, 5.0 grams; water to make 1 liter; pH, 8.5.

The shapes of the silver-*vs.*-time curves for the two exposure temperatures are distinctly different. The curves for the exposures made at room temperature show a pronounced induction period before the straight-line portion is reached, whereas the curves for the exposures made at −196°C are substantially straight lines from the very start of development. The tone of the silver image formed by incomplete development likewise is different for the two exposure temperatures. Figure 10 gives a plot of the density ratio, $D(400\ m\mu)/D(700\ m\mu)$, as a function of the amount of developed silver. The ratio for the room-temperature exposure shows the customary decrease with increasing degree of development (increasing amount of silver), whereas the ratio for the −196° exposure is smaller and nearly independent of the degree of development. The covering power of the developed silver, in terms of $D(400\ m\mu)/Ag$, was nearly independent of the degree of development of the latent image formed by exposure at −196°C, whereas it decreased steadily with increasing degree of development of the image formed by exposure at 23°C. The covering power in terms of $D(700\ m\mu)/Ag$ likewise was substantially independent of the degree of development for the low-temperature exposure, but showed only a small decrease with increasing degree of development for the room-temperature exposure.

The latent image formed by a 1-min exposure at −196°C is much more susceptible to latensification by gold than that formed at room temperature. Figure 11 illustrates the effect of gold latensification[9] on the rate of development of latent images formed at the two temperatures. The broken lines represent room-temperature exposures to a 100-w lamp and the solid lines −196°C exposures to a 500-w lamp, each exposure being made through a neutral density of 2.52 for 1 min at 80 cm. Curves 1 and 4 represent untreated samples, Curves 2 and 5 control samples bathed for 5 min in water, followed by 1 min in 0.01 *M* sodium sulfite and 5 min in 0.01 *M* potassium bromide, and Curves 3 and 6 samples gold latensified for 5 min and then treated in the sodium sulfite and potassium bromide solutions as before. The purpose of the sulfite and bromide treatment is to minimize fog. The sulfite–bromide treatment accelerates development for exposures at both temperatures, but is only slightly more effective for the low-

9. T. H. James, W. Vanselow, and R. F. Quirk, *PSA Journal*, **14**: 349 (1948).

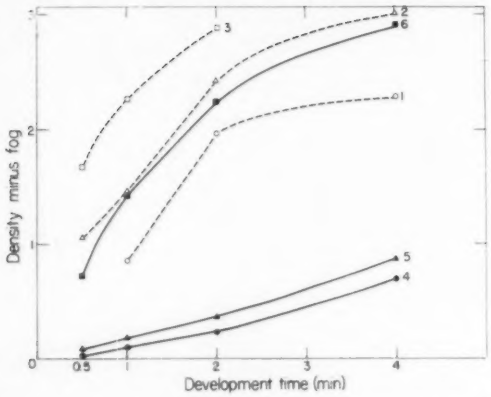

Fig. 11. Effect of latensification treatments on the rate of development of latent image formed by equivalent exposures at 23°C (broken curves) and −196°C (solid curves). Curves 1 and 4, untreated; Curves 2 and 5, sulfite-bromide controls; Curves 3 and 6, gold-latensified. D-19 development at 20°C.

temperature exposure. The gold latensification, on the other hand, increases the rate of development of the latent image formed at −196°C by several-fold whereas it increases the rate of development of the latent image formed at room temperature by less than twofold.

Discussion

An exposure at sufficiently low temperature has been considered[10] to be in effect a very-high-intensity exposure, regardless of the actual intensity. In our experiments, latent image formed at −196°C shows certain characteristics of latent image formed by a very-high-intensity exposure at room temperature.

For an exposure made at −196°C with sufficient energy to make substantially all the grains developable, the rate of surface latent-image development in the early stages is lower by about one order of magnitude than the rate of development of latent image formed by an equal exposure made at 23°C. When the exposures are adjusted to energy levels such that the characteristic curves obtained on prolonged development approximately coincide, the rate of growth of density in the early stages of development of the latent image formed at the low temperature likewise is much less than that of the latent image formed at room temperature. Cabannes[11] and Hofmann[12] observed an analogous, but less striking, decrease in the rate of development with increasing intensity of exposures made at room temperature. Our results can be explained in terms of the formation of larger latent-image centers at the higher temperature, and the "Cabannes-Hofmann" effect can be explained by the formation of larger latent-image centers at the lower exposure intensities. The analogy between the low-temperature and the high-intensity room-temperature exposure extends also to the effect of gold latensification. Latent image formed by high-intensity exposures at room temperature is more susceptible to gold intensification than that formed by low-intensity exposures,[9] and the latent image formed at low temperature is much more susceptible to gold intensification than that formed at room temperature.

Most of the latent-image centers formed at −196° C may be of threshold or near-threshold size even at the higher exposure levels where substantially all grains are developable. The latent image shows characteristics of that formed at normal temperatures by exposures at the toe level of the characteristic curve, where relatively few grains are made developable and the latent-image centers probably are of threshold or near-threshold size. The activation energies are about the same for the two cases, and the constancy of the covering power and relative spectral neutrality of the silver deposit obtained for both indicate that the increase in density with increasing time of development is due primarily to an increase in the number of relatively completely developed grains.

The present results serve to emphasize the importance of the development factor in determining the effect of temperature on the sensitivity of photographic emulsions. Because of the marked difference in development rates, the relative speeds of the same material exposed to the same intensity and quality of light at room and at liquid-nitrogen temperatures depends upon the duration of development. As the time of development is increased, the difference in speeds becomes smaller. At temperatures slightly above that of liquid nitrogen, e.g., at −186°C, the dependence of speed and gamma upon the intensity of the exposure also varies with the time of development. For short-duration development, high-intensity reciprocity-law failure is observed. However, the data for prolonged development do not indicate reciprocity failure.

The increase in the rate of development of the latent image formed by the 1-min moderate-to-high-energy level exposures as the temperature of exposure increases from −196° to −178°C indicates that the latent-image centers grow larger the higher the temperature. This indication has interesting theoretical implications. It is generally assumed that only electronic processes take place in this low-temperature region, since the interstitial silver ions are effectively "frozen in." Silver centers, according to this view, form only when the emulsion warms up prior to development. It is possible that the efficiency of trapping of electrons increases with temperature in the −196° to −178°C range and that therefore fewer electrons are lost by recombination.[3] This would mean that more electrons are available for growth of latent-image centers during the warm-up stage preceding development. How-

10. Cf. C. E. K. Mees, *The Theory of the Photographic Process*, rev. ed., Macmillan, New York, 1954, p. 233.
11. J. Cabannes and Y. Rocard, *La diffusion moléculaire de la lumière*, Les Presses Universitaires de France, Paris, 1929, p. 83.
12. P. O. Hofmann, *Physik. Z.*, **36**: 650 (1935).

ever, the substantial coincidence of the characteristic curves obtained by prolonged development of the exposures made at −196°, −186°, and −178° shows that the number of developable grains for ultimate development is the same. It might be expected that, if the number of electrons lost by recombination is substantially different at the three temperatures, some difference would be observed in ultimate speed. Moreover, an effect of temperature of exposure on the rate of development is not observed over the −196° to −178° C range when the duration of exposure is only 0.5 msec and the intensity is much higher. If recombination of electrons and positive holes is the important factor determining the difference in the rates of development of 1-min exposures made at the different temperatures, we should have to assume that no such difference exists in the number of electrons lost by recombination when the exposure is completed in 0.5 msec.

It might also be assumed that the rate of formation of photoelectrons influences the depth of subsequent trapping at the low temperatures in such a way that, on warming up the film, the rate of release of electrons from temporary traps depends on the temperature of trapping for a 1-min exposure but not for a 0.5-msec exposure. In that event, the rate of build-up of favored latent image centers might be different, but the basic assumption seems improbable.

An alternative assumption is that a further step in latent-image formation beyond the trapping of electrons can take place at temperatures slightly above −196°, and possibly even at that temperature, within a period of 1 min. One possibility is that silver ions in the immediate vicinity of the electron traps can be neutralized by the electrons within the 1-min period. Thus, a silver development center actually may start to form before the film is warmed up. The formation of even a single silver atom at a given center during a low-temperature exposure would give that center a definite advantage for subsequent growth since it would permit another electron to be trapped at that site during the exposure. Surface silver ions, which may retain some mobility at the low temperatures,[13] may even be involved.

13. J. F. Hamilton and L. E. Brady, *J. Applied Phys.*, **30**: 1893 (1959).

• Coming Technical and Scientific Meetings

Professional Photographers of America, Annual Exposition of Professional Photography, July 30–August 4, Statler-Hilton, New York

American Rocket Society, Guidance and Control Conference, August 7–9, Stanford University, Stanford, Calif.

Society of Photographic Instrumentation Engineers, Annual Technical Symposium, August 7–11, Ambassador Hotel, Los Angeles, Calif.

Biological Photographic Association, Inc., August 21–24, Chicago, Ill.

International Conference on Photoconductivity, August 21–24, Cornell University, Ithaca, N.Y.

Electron Microscopy Society, August 25–September 5, Philadelphia, Pa.

International Congress of Radiology, August 26–September 1, Montreal, Que.

American Chemical Society, 6th International Conference on Coordination Chemistry, August 27–September 1, Wayne State University, Detroit, Mich.

Inter-American Congress of Radiology, September 3–10, São Paulo, Brazil

Institute of Radio Engineers, PGIT, International Symposium on Transmission and Processing of Information, September 6–8, Massachusetts Institute of Technology, Cambridge, Mass.

International Congress for Scientific Photography, September 11–17, Zürich, Switzerland

American Roentgen Ray Society, September 26–29, Deauville Hotel, Miami Beach, Fla.

90th Semiannual Convention, Society of Motion Picture and Television Engineers, October 2–6, Lake Placid, N.Y.

American Society of Photogrammetry, Semiannual Meeting, October 4–6, Biltmore Hotel, New York. K. E. Reynolds, Chairman, Meetings Committee; Sumner Irish, Chairman, Technical Programs Committee

American Photoengravers Association, October 8–10, Penn-Sheraton, Pittsburgh, Pa.

Optical Society of America, October 18–20, Biltmore Hotel, Los Angeles, Calif.

International Symposium on Photoelasticity, October 29–31, Chicago, Ill.

Society of Reproduction Engineers, Visual Communications Congress, December 1–4, Hotel Biltmore, Los Angeles, Calif.

91st Semiannual Convention, SMPTE, April 30–May 4, 1962, Ambassador Hotel, Los Angeles, Calif.

1962 Annual Conference, SPSE, May 7–11, Somerset Hotel, Boston, Mass.

92nd Semiannual Convention, SMPTE, October 22–26, 1962, Drake Hotel, Chicago, Ill.

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Enhancement of Print-Out Effect by Bathing Treatment

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To increase the print-out effect, a bathing treatment was applied to a motion-picture positive film. Treatment was successful with solutions containing silver nitrate, sodium sulfite, sodium nitrite, sodium azide, triethanolamine, or any of several organic reducing agents. The bathing treatment results in a high-speed print-out film which is suitable for high-level radiation dosimetry, making possible the determination of 10^5 to 10^7 roentgens of gamma-rays.

The print-out effect in silver halide emulsions depends on several factors in emulsion making, especially on the composition. However, the print-out effect is also affected by bathing treatment, a process resembling bathing hypersensitization. The present paper describes a method of enhancing the print-out effect by bathing the emulsion in solutions of metal salts, sulfur compounds, nitrogen compounds, amines, organic reducing agents, or organic acids. An application of this method is the use of print-out emulsion for high-level radiation dosimetry.

Experimental Procedure

A motion-picture positive film was immersed in the bathing solution for 5 min at 20°C, then bathed in ethanol for 1 min and dried quickly. To determine the sensitivity of the film, an optical wedge for sensitometric use was attached to a test film and exposure was made to a tungsten lamp having an intensity of 1482 candles (color temperature 3000°K) for 3 min at a distance of 25 cm from the light source. The density of the print-out image was measured directly by an Ansco Densitometer of the transmission type.

The characteristic curves shown in the figures were obtained by plotting as ordinate the increase in density due to the print-out silver. The density of the unexposed motion-picture positive film, 0.64, was always subtracted from the measured density values.

Experimental Results

Metal Salts

Figure 1 illustrates results obtained when film strips were treated with thallium nitrate solutions, silver nitrate solutions, and silver tungstate solutions. The reagent concentrations are indicated on the curves. The tungstate stock solution was prepared by adding excess sodium tungstate to 4 cc of 1% silver nitrate solution; the silver tungstate precipitate was then washed and dissolved in aqueous ammonia solution, using the minimum quantity of ammonia necessary for dissolution. This solution was diluted with water to make 500 cc.

All these bathing treatments produced an increase in the print-out effect, the largest increase being caused by the silver nitrate solutions. Mercuric chloride solution was also examined, but was found to be ineffective.

Sulfur Compounds

Bathing solutions were prepared with sulfur compounds such as thiourea, allylthiourea, sodium thiosulfate, potassium thiocyanate, and sodium sulfite. Results of these treatments are shown in Fig.

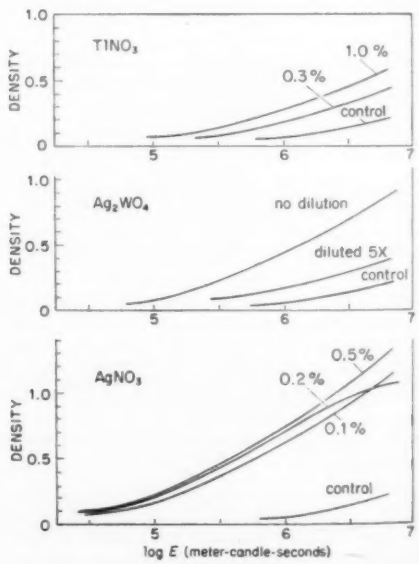

Fig. 1. Effect of treatment with metal salt solutions.

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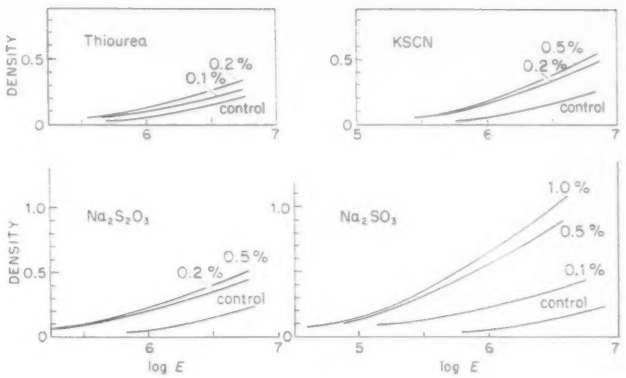

Fig. 2. Effect of treatment with solutions containing sulfur compounds.

2. Because these reagents dissolve silver halide grains the concentration of the solutions must be kept below a certain limit: less than 0.2% for thiourea and allylthiourea, 0.5% for sodium thiosulfate and potassium thiocyanate, 1.0% for sodium sulfite. The most effective reagent is sodium sulfite. Allylthiourea solutions had almost no influence on the print-out sensitivity.

Nitrogen Compounds

Solutions of aqueous ammonia, sodium nitrite, and sodium azide were used for bathing treatment. As shown in Fig. 3, these treatments increased the print-out effect. Solutions of amines also were examined, using pyridine, hydroxylamine sulfate, triethanolamine, methylamine, and dimethylamine. An enhanced print-out effect was obtained with triethanolamine, but the others were less effective, as may be seen in Fig. 4. Results for methylamine and dimethylamine are not shown; the effect was small.

Organic Reducing Agents

In Fig. 5, it may be seen that Metol, hydroquinone, resorcinol, and catechol in bathing solutions are quite effective for enhancing print-out in the emulsion.

Organic Acids

Print-out emulsions are often prepared with silver halide together with organic acid such as citric acid or oxalic acid in the presence of excess silver nitrate. To test the effect of these acids, bathing solutions were prepared with formic acid, oxalic acid, and citric acid in concentrations of 0.3 to 3.0%, and the print-out behavior was observed after the treatment. In

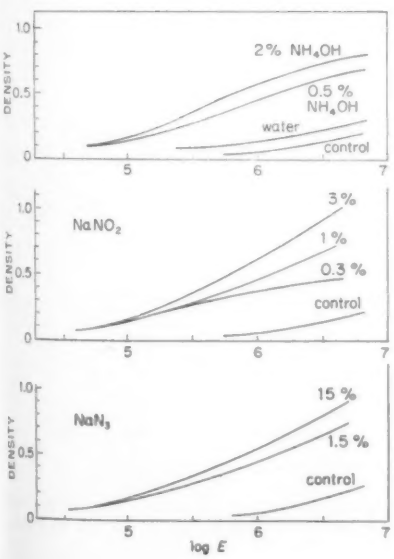

Fig. 3. Effect of treatment with solutions containing nitrogen compounds.

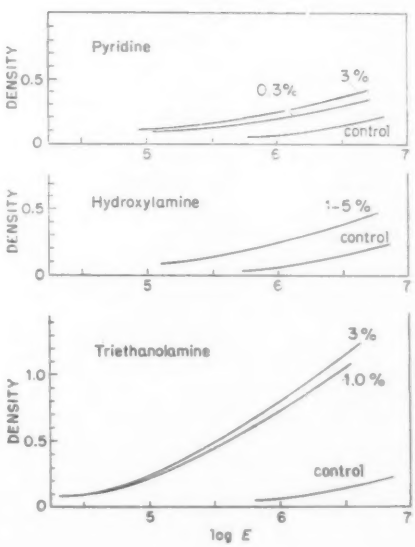

Fig. 4. Effect of treatment with solutions containing amines.

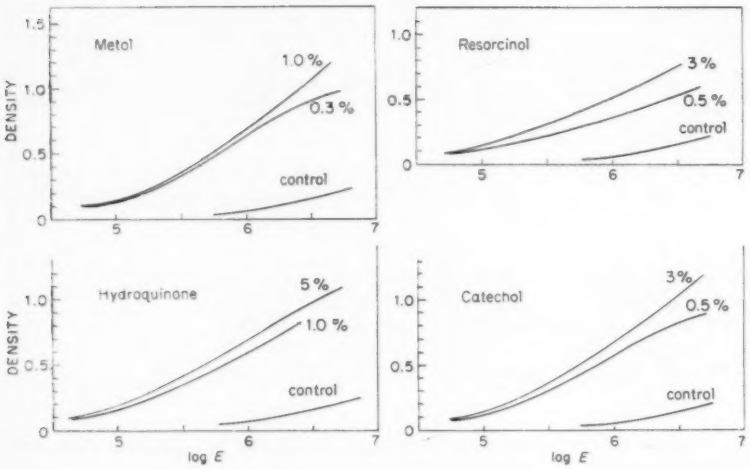

Fig. 5. Effect of treatment with solutions containing organic reducing agents.

all cases, only slight changes occurred in print-out sensitivity.

Summary of Results

Table I summarizes the enhancement of the print-out effect by the various agents and also indicates the useful range of concentration.

TABLE I. Enhancement of Print-Out Effect by Various Agents and Useful Ranges of Concentration

Groups	Reagents	Effect	Concentration, %
Metal salts	$AgNO_3$	+++	0.1–0.5
	Ag_2WO_4	++	
	$TlNO_2$	+	0.3–1.0
	$HgCl_2$	0	
Sulfur compounds	Na_2SO_3	+++	0.5–1.0
	$Na_2S_2O_3$	+	0.2–0.5
	KSCN	+	0.2–0.5
	Thiourea	0	
	Allylthiourea	0	
Nitrogen compounds	NaN_3	+++	1.5–15
	$NaNO_2$	+++	1.0–3.0
	NH_4OH	++	0.5–2.0
	Hydroxylamine	+	1.0
	Methylamine	+	1.0
	Dimethylamine	0	
	Triethanolamine	+++	1.0–3.0
	Pyridine	+	0.3
Organic reducing agents	Metol	+++	0.3–1.0
	Hydroquinone	+++	1.0–5.0
	Catechol	+++	0.5–3.0
	Resorcinol	++	0.5–3.0
Organic acids	Formic acid	0	
	Oxalic acid	+	0.3
	Citric acid	+	0.3–1.0

Application to Radiation Dosimetry

Use of print-out emulsion for radiation dosimetry is reported by H. F. Nitka and D. P. Jones,[1] and by W. L. McLaughlin;[2] our previous report describes radiation dosimetry with print-out emulsions containing silver azide.[3] Emulsions in which the print-out effect is enhanced by treatment with chemical reagents also are suitable for high-level radiation dosimetry.

1. H. F. Nitka and D. P. Jones, *Nucleonics*, **15**: No. 10, 128 (1957).
2. W. L. McLaughlin, *Radiation Research*, **13**: 594 (1960).
3. Y. Tomoda, *Phot. Sci. & Eng.*, **4**: 196 (1960).

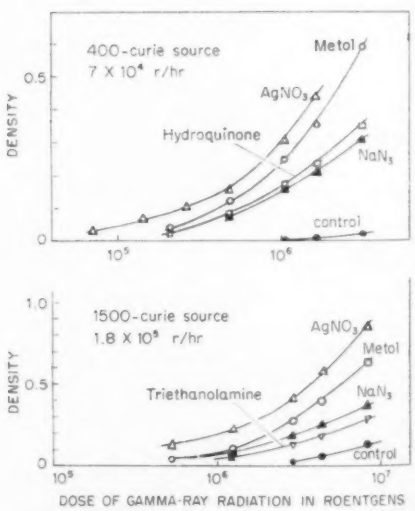

Fig. 6. Print-out characteristics of motion-picture positive film with bathing treatment, plus one untreated control, exposed to gamma rays.

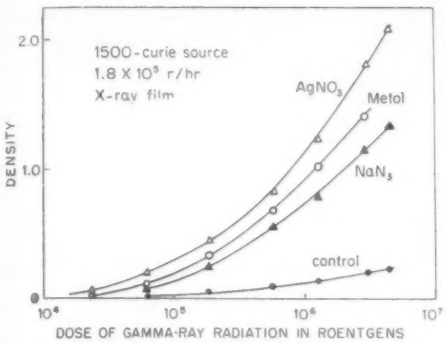

Fig. 7. Print-out characteristics of nonscreen-type x-ray film with bathing treatment, plus one untreated control, exposed to gamma rays.

Test strips of motion-picture positive film were treated with solutions of silver nitrate (0.1%), sodium azide (1.5%), Metol (0.3%), and triethanolamine (1.0%). Along with an untreated control strip, these were exposed by the time-scale method to gamma rays from two cobalt-60 sources, one a 400-curie source having a dose rate of 7×10^4 r/hr and the other a 1500-curie source having 1.8×10^5 r/hr. After exposure, print-out densities were measured. As may be seen in Fig. 6, the film without treatment gave a print-out image upon irradiation by gamma rays of a dose exceeding 10^6 r, but because of the increased print-out effect in films subjected to bathing treatment, the useful exposure range of the treated films was 10^5 to 10^7 r.

Enhancement of the print-out effect by bathing treatment also was demonstrated for nonscreen-type x-ray film. Strips of x-ray film were treated in the same way as described above, and then exposed to gamma-rays at a dose rate of 1.8×10^5 r/hr. Print-out characteristics are given in Fig. 7.

Discussion

As summarized in Table I, there are several chemical reagents which effectively enhance print-out in photographic emulsion, but the action of these reagents is not always similar. Bathing with metal salt solution causes adsorption of metal ions on the surface of the silver halide grains and forms a favorable state for deposition of metallic silver during the exposure. Treatment with silver nitrate solution is most effective and gives a print-out image brown-black in color.

The largest increase in print-out effect caused by sulfur compounds was observed with sodium sulfite solutions. In this case, the reducing action of the sodium sulfite must contribute to the formation of print-out silver. Sodium sulfite is an effective halogen acceptor, reducing the halogen to halide ion. For this reason, photolytic efficiency may be increased.

Among nitrogen compounds, sodium nitrite greatly enhanced the print-out effect. Like sodium sulfite, it acts as a halogen acceptor, reacting with halogen which is liberated from silver halide during exposure. Treatment with sodium azide or triethanolamine also gives excellent print-out enhancement, but the action of these agents has not yet been explained.

Most of the organic reducing agents used in the present studies are suitable for bathing solutions, and the print-out effect is remarkably increased by the treatment. E. A. Sutherns reported recently that the print-out of silver iodide emulsion was increased by addition of hydroquinone, pyrogallol, etc., to the emulsion[4] and this result agrees with ours.

4. E. A. Sutherns, *J. Phot. Sci.*, 8: 118 (1960).

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The Effect of Chemical Sensitization on Spectral Sensitization

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The relative spectral sensitivities of emulsions differing only in chemical sensitization were compared and found to be the same. Two emulsions were used, each with no chemical sensitization, sulfur sensitization, and sulfur-plus-gold sensitization, and five spectral sensitizations were used with each emulsion and type of chemical sensitization. The results show no indication that intermediate energy levels which may be produced by chemical sensitization interact differently with sensitivity in the region of silver halide absorption and in the region of dye absorption.

In all cases of spectral sensitization, in the photographic emulsion or in other systems, a photochemical reaction is brought about by quanta smaller than those absorbed by the reacting material, or at least by quanta of radiation which are very weakly absorbed. As a concrete example, if it is assumed that the long-wavelength limit of absorption in a silver halide emulsion represents the minimum energy necessary to set free an electron, quanta absorbed by a sensitizing dye must be supplemented in some way if they are to produce a latent image. It should be said at this point that the assumption is believed to be incorrect, on the basis of evidence in the literature and of that presented in this paper, but it has been widely made and should be discussed. Thermal activation is one of the conceivable sources of supplementary energy, but this hypothesis can be eliminated because the data on the temperature coefficient of sensitization[1] are in disagreement with it.

The explanations most generally offered for spectral sensitization in silver halide emulsions depend, in one way or another, on the existence in the crystal of energy levels above the average, at defects, or simply on the surface. It has been suggested that either the quanta absorbed by the dye can raise electrons from these defect levels to the conduction band, or electrons may be transferred directly from the excited dye molecules to the conduction band, following which the dye molecules recover electrons from the defect levels.[2,3] The question of how the defect levels are replenished to permit the process of image formation to go on has not been answered. However, on either basis, chemical sensitization might interact with spectral sensitization because it alters the energy levels in the grain, and there is the obvious possibility that, because of the introduction of new energy levels by chemical sensitization, spectral sensitization might become more efficient. It is significant that there has been no difficulty in sensitizing sheet crystals of silver bromide by bathing in dye solutions, so that a high degree of structural perfection is compatible with spectral sensitization.

Direct comparisons of spectral sensitization by dyes in emulsions without and with chemical sensitization have been reported by Sheppard[4] and by Carroll and Hubbard,[5] neither of whom found significant differences in relative spectral sensitivity as a result of chemical sensitization.

In undyed emulsions, chemical sensitization increases relative sensitivity for long wavelengths,[6–9] although the increase in sensitivity is about two orders of magnitude less than can be obtained by sensitization with dyes. The change in spectral absorption can be detected only in very transparent emulsions,[7] and the evidence is not adequate to show the relation between increase in absorption and increase in sensitization. If intermediate energy levels, corresponding either to chemical sensitization or to the dislocations which can be detected in emulsion grains by x-ray analysis,[9] could increase effectiveness of long-wavelength sensitization by dyes, it seems reasonable to assume that there should be a similar effect at the long-wavelength edge of absorption by silver halide. However, Dickinson[8]

Communication No. 2194 from the Kodak Research Laboratories. Received 9 June 1961.

1. W. West, "The Temperature-Dependence of Spectral Sensitization by Dye Series of Regularly Increasing Chain Length," paper presented at the 1961 Annual Conference, Binghamton, N.Y.
2. N. F. Mott, *Phot. J.*, **88B:** 119 (1948).
3. J. W. Mitchell, *Reports of Progress in Physics*, **20:** 433 (1957).
   J. Eggert, *Ann. Physik*, (7)**4:** 140 (1959).
4. S. E. Sheppard, *Colloid Symposium Monograph*, **3:** 1 (1925).
5. B. H. Carroll and D. Hubbard, *Bureau of Standards Research Paper 488; Bur. Standards J. of Research*, **9:** 529 (1932).
6. J. Eggert and M. Biltz, *Trans. Faraday Soc.*, **34:** 892 (1938).
   J. Eggert and F. G. Kleinschrod, *Z. wiss. Phot.*, **39:** 155, 165 (1940).
7. K. V. Chibisov, *J. Phot. Sci.*, **7:** 41 (1959).
8. H. O. Dickinson, *ibid.*, **7:** 105 (1959).
9. R. H. Herz, *J. Phot. Sci.*, **8:** 2 (1960).

concluded that silver sulfide formed during chemical sensitization may be in more than one form and these forms may have different effects on total sensitivity, relative spectral sensitivity, and fog. If this is true, the relation between absorption and sensitization at the long-wavelength limit of absorption by silver halide and the sensitivity in this region tells very little about the nature of the contribution by intermediate levels. Altogether, it appeared desirable to secure more complete data on the interactions of chemical and spectral sensitization, especially in emulsions of minimum inherent sensitivity.

Experimental

Data will be presented for experiments with two emulsions, a bromoiodide of the Simplex[10] type with 4 mole % silver iodide, and a pure bromide with fine, uniform grains. In each case, the emulsions were made with an inert gelatin and, in the absence of deliberate chemical sensitization, were primitive.[11] In this state, they had extremely low sensitivity for formation of surface latent image; the bromoiodide emulsion had moderate sensitivity for internal image, and the pure bromide, extremely low. Each emulsion was divided into portions, of which one was left chemically unsensitized, one was sensitized with a sulfur compound, and one with a sulfur and a gold compound. The unsensitized Simplex emulsion was also coated with a halogen acceptor (acetone semicarbazone) to reduce possible fading of the latent image after the flash exposures; no difference was observed, and it serves as a useful duplicate. Each portion of a given emulsion with a given chemical sensitization was further subdivided, and was spectrally sensitized with cyanine and merocyanine dyes, the concentrations being adjusted according to the emulsion. The spectral absorption of each coating was measured; there were no differences within the limits of experimental error between any pair of coatings which differed only in chemical sensitization.

Relative spectral sensitivity was determined by filter exposures, since the interest was primarily in differences between coatings. A combination of Kodak Wratten Filters No. 35 and 38A was used to isolate a narrow band in the violet region absorbed only by the silver halide; this filter combination has a maximum transmission of 30.5% at 420 mμ, falling to 0.13% at 470 mμ. A Wratten Filter 16 or 12 was used to isolate the region of spectral sensitization. All exposures were to an intensity scale, for the same time for all coatings to be compared. Although the reciprocity failure of these emulsions was not determined, it may be assumed that there were differences between the chemically sensitized and the unsensitized emulsions. Comparison of the relative spectral sensitivity of two emulsions with different reciprocity-failure curves is dependent on the relation, which has been found to hold quite generally,[12] that reciprocity-failure curves of the same emulsion coating for different wavelengths are parallel when plotted on a time scale, so that all exposures of the same emulsion should be made for the same time. Exposures were made to an incandescent source in an Eastman Ib Sensitometer. The bromoiodide emulsion was also exposed to a xenon flash (about 50-μsec duration); as the spectral distribution of this source is quite different from incandescent light, the relative spectral sensitivities, measured by the filter ratios, cannot be compared with those from the Ib Sensitometer exposures of the same films. The pure bromide emulsion was too insensitive for this source. The bromoiodide emulsion was also exposed with a spectrosensitometer;[13] results were in agreement with the filter exposures, but the more limited range of exposures available made results on the unsensitized emulsions less precise.

The distribution of latent image between surface and internal image is generally the same for all wavelengths to which an emulsion is sensitive.[14] It accordingly changes with chemical sensitization; a much higher proportion of the image formed in a sulfur-sensitized emulsion will be on the surface, compared to the same emulsion in the primitive state. If the distribution of image in a given emulsion is independent of wavelength, it will not matter whether relative spectral sensitivity is measured by development of surface or internal image. However, in order not to rely on this relation, one of the emulsions (the pure bromide) was developed both with Kodak Developer D-19 and with a *p*-methylaminophenol–ascorbic acid developer without sulfite, with parallel results. The chemically unsensitized Simplex emulsion had extremely low contrast on 4-min development with the latter formula; there was no question that spectral sensitization by the dyes was of the same order as with D-19 development, but it was impossible to assign useful figures to the test results. While D-19 is normally a surface developer, the chemically unsensitized Simplex emulsion presumably had a strong preponderance of internal image, some of which may have developed in the D-19.

The data for the Simplex emulsion are given in Table I, in terms of relative sensitivities on a logarithmic scale to exposures through the filters; the relative spectral sensitivities were calculated from these values. Three spectral sensitizations were used with each chemical sensitization, two of them at two levels. Tests of the sulfur-sensitized emulsion were duplicated with 4-min development; they were also made with 8-min development in D-19, and the relative spectral sensitivities for these are given in parentheses. The unsensitized emulsion was effectively the same with and without halogen acceptor. It will be obvious that the thiacarbocyanine in-

10. A. P. H. Trivelli and W. F. Smith, *Phot. J.*, **79:** 330 (1939).
11. W. G. Lowe, J. E. Jones, and H. E. Roberts, *Fundamental Mechanisms of Photographic Sensitivity*, Butterworths Scientific Publications Ltd., London, 1951, p. 112.
12. J. H. Webb, *J. Opt. Soc. Am.*, **23:** 316 (1933). J. H. Webb and M. Biltz, *ibid.*, **38:** 561 (1948).
13. C. A. Morrison and H. O. Hoadley, *PSA Journal* (*Phot. Sci. Tech.*), **16B:** 64 (1950).
14. C. E. K. Mees, *The Theory of the Photographic Process*, rev. ed., Macmillan, New York, 1954, Fig. 87, p. 225.

TABLE I. Simplex Emulsion

First column, dyes used for spectral sensitization in milligrams dye per mole silver halide:
A. 3,3′-diethyl-9-methylthiacarbocyanine bromide
B. 1,1′-diethyl-2,2′-cyanine iodide
C. 4[(3-ethyl-2(3H)benzothiazolylidene)isopropylidene]3-methyl-1(*p*-sulfophenyl)5-pyrazolone
D. 3-carboxymethyl-5[(3-ethyl-2(3)benzothiazolylidene)ethylidene]rhodanine

Each group of three columns corresponds to a chemical sensitization: I, none; II, none, with halogen acceptor added to the emulsion; III, sulfur-sensitized; IV, sulfur-plus-gold-sensitized. In each group, V indicates sensitivity to violet light, transmitted by the Wratten Filters 35 + 38A; #16 indicates sensitivity to light transmitted by Wratten Filter 16; RSS is relative spectral sensitivity, calculated as (#16-V).

The figures are relative sensitivities, expressed as 100 (1-log $E_{0.10}$) where $E_{0.10}$ is the exposure incident on the filter which is required to produce a density 0.10 greater than fog, on 4-min development at 68°F in Kodak Developer D-19. Figures in parentheses are for 8-min development.

	I			II			III			IV		
Dye	V	#16	RSS	V	#16	RSS	V	#16	RSS	V	#16	RSS
Part 1: Exposures in Eastman Ib Sensitometer, 3000°K source, 1.0 sec												
None	−14	——	——	−14	——	——	87, 84	——	——	102	——	——
A. 75 mg	−04	68	+72	02	83	+81	102, 89	174, 168	+72, +79 (+87)	117	180	+63
A. 131 mg	+04	102	+98	04	101	+97	91, 96	178, 184	+87, +88 (+88)	107	205	+98
B. 117 mg + C. 23 mg	−22	58	+80	−11	66	+77	87, 78	160, 145	+73, +67 (+66)	104	173	+69
D. 56 mg	−08	45	+53	−18	39	+57	84, 85	116, 116	+32, +31 (+34)	89	138	+49
D. 99 mg	−08	58	+66	−08	62	+70	75, 80	115, 130	+40, +50 (+49)	92	152	+60
Average			+75			+76			+63			+68
Part 2: Exposures through step wedge to xenon flash, 50 μsec												
None	09	——	——	12	——	——	98	——	——			
A. 75 mg	17	41	+24	18	44	+26	110	133	+28			
A. 131 mg	27	66	+39	15	43	+28	120	143	+23			
B. 117 mg + C. 23 mg	20	27	+07	06	06	00	94	108	+14			
D. 56 mg	17	12	−05	12	00	−12	92	67	−25			
D. 99 mg	30	30	00	07	16	+09	85	85	00			
Average			+10			+10			+08			

creased the sensitivity of the chemically unsensitized and even the sulfur-sensitized emulsion to the violet region, by an amount greater than the probable error. This was also observed by Tamura and Hada[15] on spectral sensitization of chemically unsensitized emulsion with 3,3′-diethylthiacyanine and 3,3′-diethylthiacarbocyanine. The effect was originally observed by Lüppo-Cramer[16] with the oxazine dye, Capri Blue, and related dyes, but it may also occur with cyanines and other sensitizing dyes in unsensitized and undersensitized emulsions. Desensitization of the chemically sensitized emulsion by these dyes at the levels used was slight.

The scatter of the values of relative spectral sensitivity is relatively large, but appears to be random; accordingly, the average values of all relative spectral sensitivities for a given chemical sensitization and exposure condition, as well as the individual figures, are given in the table. The conclusion is that relative spectral sensitivity for a given dye-sensitization was independent of chemical sensitization, with the possible exception of weaker sensitization in the sulfur-sensitized emulsion; comparison of values either by pairs or by average shows that spectral sensitization was not made more efficient by chemical sensitization of the emulsion.

The relative spectral sensitivities of the unsensitized and sulfur-sensitized Simplex emulsion at the long-wavelength edge of silver halide absorption were compared in the spectrosensitometer.

The spectrosensitometer has a fixed range of intensities, in ten steps differing by a ratio of 2.00; accordingly, if two emulsions of widely different sensitivities are compared at a single exposure time, there may be only a narrow range of frequencies for

15. M. Tamura and H. Hada, papers presented at the Colloque International de Photographie Scientifique, Liège, 1959.
16. H. Lüppo-Cramer, *Z. wiss. Phot.*, **30**: 1, 241, 249 (1931).

TABLE II

Pure bromide emulsion, exposed in Eastman Ib Sensitometer for 1.0 sec to 3000°K source. Relative speeds are expressed as 100 (1-log $E_{0.30}$) where $E_{0.30}$ is the exposure required to produce a density 0.30 greater than fog on development at 68°F for 3 min in D-19 or 4 min in surface developer. #12 indicates exposure through Wratten Filter 12; other symbols for chemical sensitization and exposure conditions are the same as in Table I.

Chemical sensitization	Dye	3 min in D-19			4 min in surface dev.		
		V	#12	RSS	V	#16	RSS
I	None	−206	——	——	−203	——	——
	A. 163 mg	−188	−50	+138	−184	−67	+117
	A. 286 mg	−189	−43	+146	−176	−46	+130
	B. 256 mg + C. 50 mg	−196	−68	+128	——	——	——
	D. 121 mg	−172	−44	+128	−166	−50	+116
	D. 213 mg	−171	−27	+144	−163	−38	+125
	Average			+137			+122
III	None	−182	——	——	−162	——	——
	A. 163 mg	−167	−34	+134	−164	−42	+122
	A. 286 mg	−175	−34	+141	−162	−48	+114
	B. 256 mg + C. 50 mg	−148	−13	+135	−139	−16	+123
	D. 121 mg	−124	+14	+138	−114	−01	+113
	D. 213 mg	−131	+06	+137	−120	+08	+128
	Average			+137			+120
			#16				
IV	None	−65	——	——	−67	——	——
	A. 163 mg	−65	+45	+110	−87	+03	+90
	A. 286 mg	−70	+58	+128	−100	+16	+116
	B. 256 mg + C. 50 mg	−63	+59	+122	−82	+32	+114
	D. 121 mg	−45	+55	+100	−62	+51	+113
	D. 213 mg	−48	+85	+133	−65	+62	+127
	Average			+113			+112

which both are correctly exposed. This was the case for the unsensitized and sulfur-sensitized Simplex emulsion; when these coatings were exposed at the normal rate of operation of the spectrosensitometer, sensitivities could be adequately compared over the range from 510 to 540 mμ; by modifying the operation so that exposures of 16 sec were given at each wavelength, comparisons could also be made from 540 to 560 mμ. The ratio of sensitivities did not change significantly between 510 and 560 mμ; the ratios are plotted in Fig. 1 as the difference in the logarithms of the intensities required to produce a density of 0.05 over fog.

The spectral sensitivity of the sulfur-sensitized emulsion could be followed to 610 mμ (Fig. 2). At 560 mμ, there was a change in slope similar to that found at 560 mμ by Eggert and co-workers[6] for an emulsion with the same proportion of iodide. It was impossible to compare this with changes in spectral absorption of the emulsions, as the absorption of turbid emulsion coatings such as these could not be measured to less than 1%, and the sensitivity of the emulsions at wavelengths past 560 mμ is much less than 1% of that at 400 mμ. The absorptions of the unsensitized and sulfur-sensitized emulsions were the same, within the limits of experimental error.

Results with the fine-grained pure bromide emulsion are reported in Table II. This emulsion was much slower and had high contrast, even with surface development in the unsensitized state, so that a

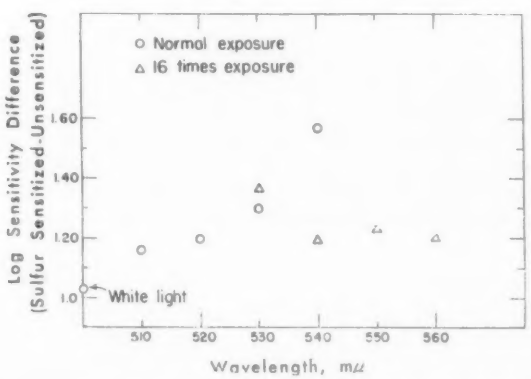

Fig. 1. Ratio of sensitivities of sulfur-sensitized and unsensitized Simplex emulsion at the long-wavelength edge of sensitivity. The ratio, plotted as the logarithm of the sensitivity difference, is plotted against wavelength.

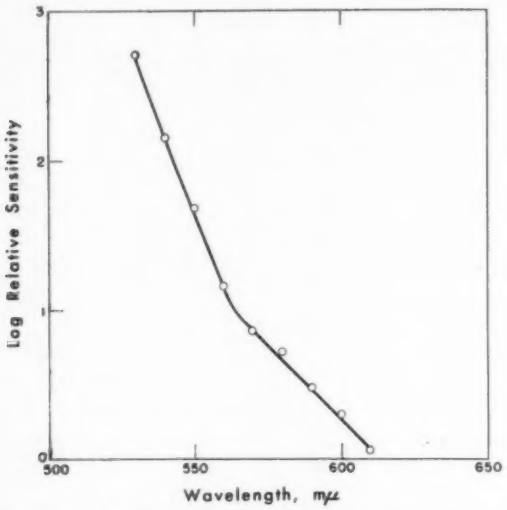

Fig. 2. Spectral sensitivity curve of the undyed sulfur-sensitized Simplex emulsion, showing characteristic "break" at 560 mμ.

density of 0.30 was chosen for the exposure index after comparison of results with lower and higher values. Data are given for both D-19 and surface development. This emulsion increased in speed for exposures with Wratten Filters 35 + 38A on addition of dyes ("Capri Blue effect"), especially the merocyanine dye, D. The thiacarbocyanine dye A increased the sensitivity of the chemically unsensitized emulsion to violet light, and decreased the sensitivity of the sulfur-plus-gold-sensitized emulsion to this region; the effect on the sulfur-sensitized emulsion was very slightly negative, corresponding to its intermediate sensitivity.

Two of the groups of this emulsion were tested only with the Wratten Filter 12 and D-19 development. These may be compared with each other; all three groups may be compared with the Filter 16 and surface development; and the sulfur-and-gold-sensitized emulsion may be compared with the Filter 16 and both developers. The much higher values of relative spectral sensitivity compared to those of the first emulsion result not only from the higher dye concentrations which could be used with the finer grains, but also because the pure bromide has materially less absorption of light transmitted by the combination of Wratten Filters 35 + 38A.

The data show no trend in relative spectral sensitivity with chemical sensitization, by comparison of appropriate pairs of coatings, and the average values are satisfactorily constant.

Conclusions

The sensitivity of two emulsions to light in the region of spectral sensitization was increased by chemical sensitization in the same proportion as sensitivity to light absorbed by the silver halide, and no more. A similar relation was found for sensitivity to light of different wavelengths absorbed by the silver halide. Furthermore, it is known that the change in distribution of latent image between the surface and the interior of the grains produced by chemical sensitization is the same for both regions. It is impossible to say that spectral sensitization by typical dyes might not fail to function at more complete perfection of the silver halide crystal, but since it functions in highly perfect sheet crystals and primitive emulsions, it is very unlikely that this hypothetical degree of perfection could be reached in emulsion experiments.

It is generally accepted that chemical sensitization introduces new defects into the emulsion grains, or increases the effective trap depth of those already present. However, any resulting changes in spectral sensitivity of latent-image formation or of photoconductivity are of a widely different order of magnitude from those produced by dye-sensitization, and the primary function of chemical sensitization may be described as an increase in the probability that photoelectrons will combine with silver ions instead of recombining with positive holes. If this is the case, it should function as well for photoelectrons coming from absorption in one region as in another, as is actually the case.

It seems logical to suggest that any theory of spectral sensitization should begin by accepting as an experimental fact that the primary process of latent-image formation is no more dependent on participation of intermediate energy levels when the light is absorbed by a typical sensitizing dye than when it is absorbed by the silver halide. Expressing it in another way, the absorption edge of the silver halide does not indicate the minimum quantum capable of causing an electron transition to the conduction band, a conclusion which is reinforced by the existence of spectral sensitization in noncrystalline systems where the presence of intermediate energy levels resulting from crystal defects cannot be invoked.

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The Kalvar Process

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The Kalvar process, a low-speed heat-developed light-scattering photographic system, is described. The maximum sensitivity is in the ultraviolet region, with a sensitivity tail extending into the visible. The reciprocity law is valid in the exposure time range 0.05–60 sec. Latent-image stability is discussed. The material can be fixed after development, if desired. Image density markedly depends on the viewing conditions. The ratio of projection to diffuse density is high, and a reversal of the image from positive to negative can be observed in a transparency by changing the angle of incidence of the illuminating light. Applications of Kalvar materials are discussed.

Kalvar photographic materials consist of a thermoplastic resin coated on either a transparent backing material, usually Mylar, or on an opaque black paper. Within the layer of thermoplastic resin, normally slightly less than 0.0005 in. thick, a light-sensitive diazonium salt is uniformly dispersed. This salt decomposes upon exposure to ultraviolet radiation, releasing nitrogen and other volatile fragments which collect in small nucleating centers. Upon subsequent heating, the gas expands to form microscopic vesicules. Because they have an index of refraction different from that of the surrounding medium, these vesicules scatter light incident upon them and thus form the image (Fig. 1).

The light-scattering elements can vary from 0.5 μ to 5 μ in diameter. They are embedded in a hydrophobic plastic and consist of cavities surrounded by a shell of more highly ordered, crystallike material than the surrounding medium. Unlike bubbles which might be formed in gelatin by a similar method, they are highly resistant to changes in temperature and humidity. A normally developed image will withstand 4 hr storage at 150°F without substantial deterioration. Raw Kalvar material may generally be stored at any temperature below 110°F without precautions against the effects of variations in humidity.

The image opacity, or density, in a Kalvar film depends on the reflection and refraction of the incident light instead of on the absorption of that light. When an image on a transparent base is viewed in reflected light, the exposed areas, which contain the light-scattering elements, appear white and the unexposed areas appear dark. On the other hand, when this same image is viewed by transmitted light, the areas containing light-scattering elements appear dark, while the clear areas appear white. Thus Kalvar film is a reversal material when viewed with transmitted light, although Kalvar paper, with the coating on a black opaque base, is viewed only by reflected light and is a direct positive material.

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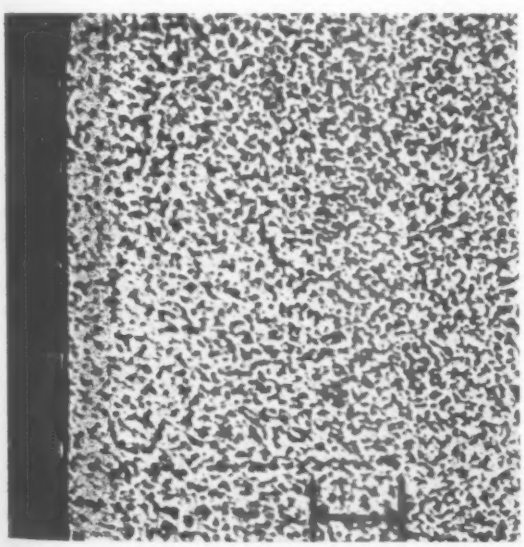

Fig. 1. Image structure of Kalvar films. 10 μ between marks.

Sensitivity

Kalvar is a comparatively low-speed material, with its primary sensitivity in the near ultraviolet (Fig. 2). Its maximum photosensitivity, when de-

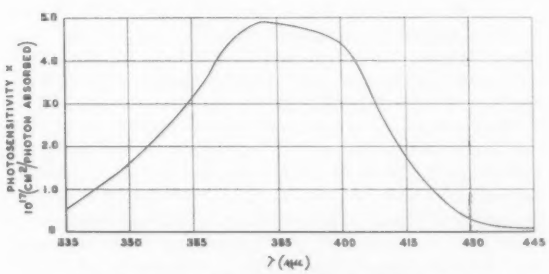

Fig. 2. Spectral photosensitivity of Kalvar films.

fined as the product of the extinction coefficient and the quantum yield, is at 385 mμ. The amount of radiation required to produce maximum density at this wavelength is about 200 mw-sec/sq cm.

Short-arc mercury vapor lamps which have a high intrinsic brightness, coupled with a desirable spectral output, are the most efficient sources of exposure, but black-light fluorescent tubes, carbon arc lamps, and tungsten lamps are usable when longer exposure times are not objectionable. A 300-w tungsten projection bulb, used with a condenser, will expose Kalvar film, through an average continuous-tone negative, in 10 to 15 sec.

Exposure to radiation in the narrow region between 360 and 400 mμ will produce images of higher resolution and sharpness than exposure to the full spectral range of a tungsten lamp because the extinction coefficient is lower for radiation above 400 mμ. When the extinction coefficient is low, the light which is scattered in the layer or otherwise deflected from its path penetrates further into the layer and produces a lower edge gradient. Scattered radiation for which the extinction coefficient is high will not spread so far. For the same reason, halation effects will also be more pronounced when the extinction is low. The decrease in resolution referred to is only of importance in applications requiring resolution above 150–200 lines/mm.

Reciprocity Characteristics

The reciprocity law is valid over a large range of exposure times; gamma and speed remain practically constant over exposure times from 0.05 to 60 sec, an intensity range of 1 to 1200. Exposures longer than 60 sec are useful, but the density obtained is no longer proportional to the exposure time. Exposures lasting longer than 5 min are not advisable unless made at low temperatures. For very short exposure times there is a slight gain in the maximum density obtainable; for the longest exposure times, a slight loss occurs because some of the gas generated escapes.

Development and Fixation

Kalvar materials are developed by the application of heat. The method by which heat is applied is not critical. A common method uses a belt-driven heated roller over which the film is passed. For small areas, where the problems of uniform contact are more easily solved, a heated platen is excellent. Infrared radiation also can be used.

Both time and temperature of development can be varied within fairly wide limits without critically affecting the photographic characteristics. An average development cycle consists of placing the film in intimate contact with a heated rubber-covered metal roll for 0.5 sec at 235°F. Satisfactory development can be obtained at temperatures ranging from 180°F to over 300°F in times ranging from milliseconds to

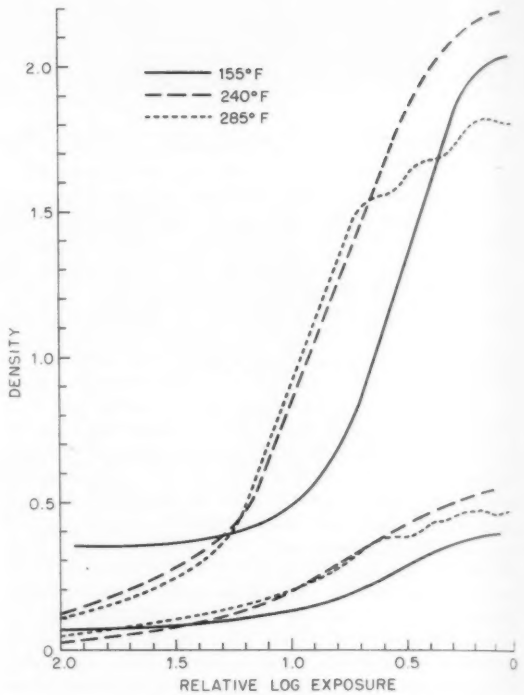

Fig. 3. Variations in development at three different temperatures. Development time, 2 sec. The lower set of three curves represents diffuse densities, the upper set projection densities. The values on the abscissa refer to the densities of the silver wedge through which the exposure was made.

over 5 sec (Fig. 3). In general, a higher temperature of development, for a given time, produces a more permanent image, lowers the resolution, and creates larger light-scattering elements. A longer time of development, for a given temperature, lowers both the resolution and sharpness.

If the specific application so requires, Kalvar materials can be "fixed," i.e., converted to a state which is no longer affected by light. Since, after development, those areas which were not exposed still contain undecomposed sensitizer, they can be fogged by subsequent exposure and heat. Thus the fixing process is designed to decompose completely the residual sensitizer and consists of a deliberate over-all exposure to ultraviolet, about two times as long as required for a maximum image-forming exposure. Following this, the film is kept at below 110°F for several hours to permit the gas to diffuse completely from the film. Fixing is not necessary when the developed film can be protected from either exposure to ultraviolet or exposure to elevated temperatures. As a general rule, the higher the temperature of development, the higher will be the temperature the unfixed film can withstand without fogging.

Latent Image Stability

Since the Kalvar latent image is comprised of a given amount of gas, it has a finite decay time which depends on the permeability of the thermoplastic to nitrogen. The decay time can be adjusted by adding modifiers to the basic vehicle resin to increase or decrease its permeability. Exposure to ultraviolet at a temperature slightly below that temperature at which fogging would occur will decrease the decay time. This decrease is desirable in applications where the film is subjected to elevated temperatures soon after exposure and development. On the other hand, in some particular applications it is desirable to expose different portions of the film during a prolonged period, and it is important to prevent diffusion of the nitrogen within this period in order to retain maximum image-forming potential. In normal Kalvar film, it takes approximately 8 hr for the gas to escape completely. With a more permeable film at an elevated temperature, this time can be a matter of seconds. Kalvar films have been produced in which no decrease in the maximum obtainable density occurs within a period of 30 min. Usually, it is best to develop the film within 3 min after its exposure has been completed.

Characteristic Curve and Viewing Conditions

The characteristic curve of a Kalvar film depends on the way in which the image is viewed. The characteristic curve for diffuse densities has an average gamma of 0.35 and a density range of about 0.60 density units, indicating a low-contrast material with a limited density range. However, when the effective density is measured in a projection system where the film sample is illuminated by collimated light and where the projection lens gathers the transmitted light over a solid angle corresponding to a relative aperture of $f/4.0$, the density range is extended to over 2.0 density units and the gamma is greatly increased. Thus the ratio between projection and diffuse density is quite high for Kalvar light-scattering films. This may be explained by the fact that a substantial portion of the light scattered is scattered in a forward direction, and falls outside of the acceptance angle of the projection lens. Hence, the measured density strongly depends on the solid angle subtended by the light-gathering element (see Fig. 4).

When the principle of optical reversibility is taken into account, a further consequence of attenuation of the incident light by scattering is that the density range and contrast of a given image depend on the incidence of the illuminating light. If it is illuminated by normally incident light, a Kalvar transparency presents the viewer with a high-contrast image. When the average angle of incidence of the illuminating light is varied from the normal, the contrast of the image and the density range become lower as the angle is increased, and a point is eventually reached at which the photographic field becomes almost neutral; there is no, or very little, contrast

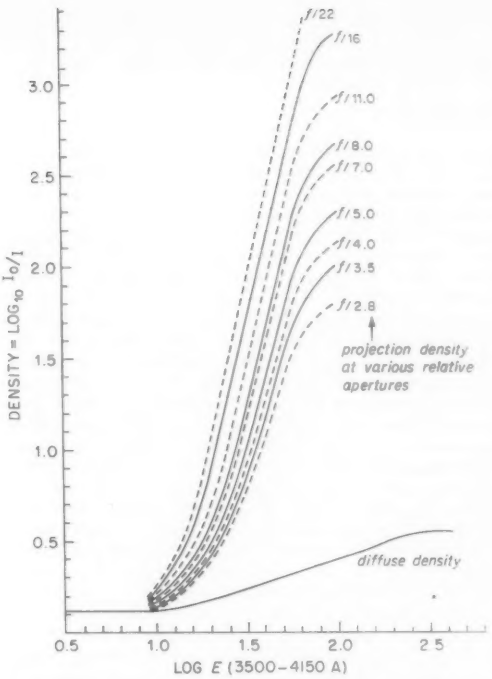

Fig. 4. Characteristic curve — projection and diffuse density vs. log exposure. Film type, Kalvar 7BTC. Exposure, 40 sec at 350–415 mμ.

visible. Increasing the angle beyond this point will change the "photographic sign" of the transparency. A positive will turn into a low-contrast negative, and as the angle is still further increased the negative will gain in contrast. An instantaneous reversal can be obtained by changing the illumination rapidly from normal incidence to a large average angle of incidence.

Resolution and Sharpness

Kalvar materials are potential high-density information storage media, capable of achieving resolution on the order of 500 lines/mm. The measurement of resolution in lines per millimeter is not, however, an adequate standard to determine the enlargement qualities of an image reduced to 1/50–1/60th its original size. To obtain a more reliable standard for determining the quality of a highly reduced image from which subsequent enlargements are to be made, the film sample is exposed to a knife edge. The net diffuse density of the sample, divided by the width of the transition area between the dense and the clear areas multiplied by a constant, gives a sharpness number for Kalvar which corresponds very closely to the subjective evaluation of the readability of an enlargement made from the image in question. The resolution characteristics of Kalvar material may be judged from the fact that

more than three generations of contact prints may be made on Kalvar film, maintaining an original maximum resolution of 228 lines/mm.

Applications

At the present time, the primary use of Kalvar films is in microfilm reproduction and in information storage and retrieval systems. The short heating time required to develop Kalvar materials, of the order of milliseconds, suggests their use in high-speed recording and rapid display systems, but we know of no high-speed recording device that supplies enough actinic energy to expose Kalvar materials. For instance, a cathode-ray tube, under optimum conditions using a P-11 phosphor, furnishes only about 1/2000th enough energy. A major advance in the actinic output of cathode-ray tubes will be required to make this type of recording possible.

Another approach to the problem of using Kalvar materials in high-speed recording and rapid display systems is to create an image by selective development of Kalvar material which has previously been uniformly exposed. A heated stylus might be used to create a dense line on such film. The writing speed of the stylus might be limited only by mechanical considerations, although the question of the rapid and efficient transfer of heat from the stylus to the film has yet to be fully explored. The friction of such a stylus at a high writing speed has been used to create heat for development.

The thermographic characteristics of Kalvar materials make them suitable to the high-speed recording of simple pulsed signals where the frequency of the pulse, as in sonar, for instance, is important. This type of signal may be recorded by using the input pulse to release the arm of a small microswitch to bring a small heated element into momentary contact with a pre-exposed piece of Kalvar material. Alternately, the film itself might be used as a diaphragm to be vibrated by the input pulse so that each vibration causes the film to come into contact with a heated wire.

In recording directly from the face of a cathode-ray tube, the primary high-speed exposure may be made on a silver halide emulsion which may then be processed in 3 or 4 sec with little or no regard for the permanence of the image obtained. Unless the intricacies of autopositive processing are introduced, this primary image will normally consist of dark lines on a light background. To obtain a negative of this image, which is often desired or required for visual presentation or enlargement to hard copy, the silver transparency can be used to produce a "negative" on Kalvar film. The complete processing time for both the silver and the Kalvar transparencies may be less than 10 sec.

The Print-A-Pix tube, manufactured by Litton Industries, offers an opportunity to record and display rapidly on Kalvar film. Using what may be called electron fibers, this tube presents a well-defined electron beam on its face. In a variation of familiar electrostatic printing techniques, this beam is ordinarily used to place a charge selectively on ordinary bond paper so that small dense particles may be attracted and bonded to the charged area. If Kalvar film instead of bond paper is used, the dense particles are attracted in the same manner to the charged areas, and, without bonding, may be used as the image-defining matrix during a normal exposure. After exposure, the charge and the particles are removed from the film, which is then developed as usual. This technique produces, in effect, a direct negative image with inherently superior projection qualities. Since the opaque particles are not bonded to the film, the resolution obtainable is higher than is possible when the particles are fused. The energy requirements for creating the proper charge on the film are small, of an order of magnitude of 0.1 mw-sec/sq cm, so that an area 2.75 by 3.5 in. can be charged in about 1/30 sec.

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• A Review

Thermal Development of Diazotype Papers

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In spite of the great success of diazotype papers in the last 30 years, there has been an interest in replacing chemical development by more convenient heat development. A search of domestic and foreign patents shows that diazotype paper developable by heat has been under study, on and off, for many years, by all important manufacturers of diazotype paper. The problem has been approached from almost every possible angle, but the absence of heat-developable diazo papers on the market is evidence of failure. There are still a few approaches, however, that have not been, or have been only very insufficiently, investigated.

Diazotype reproductions are made commercially by two processes: the Ozalid, or dry process, and the Bruning, or semidry process. Both processes are based on the ability of diazo compounds to form azo dyes with coupling components, such as amines, phenols, and aminophenols. While the credit for producing the first positive diazo prints goes to Green, Cross, and Bevan,[1*] Andressen,[2] Shoen,[3] and Ruff and Stein,[4] the first commercially successful application of diazonium compounds to the production of positive printing paper was based on discoveries of Koegel (diazonaphtholsulfonic acid),[5] van der Grinten (*p*-tertiary amino anilines),[6] and Lehmann (amino-diphenylamines),[7] more than 20 years later. Subsequently, Schmidt and Krieger,[8] disclosed the use of ortho- and para-amino-diazo compounds (*p*-dimethylamino-benzene-diazonium chloride) and more recently, Leuch[9] and Werner[10] introduced a large class of amines with other groupings, e.g., 2,5-dimethoxy-4-acetylaminoaniline.

The diazonium compounds themselves are yellow substances which decompose upon exposure to light, releasing two nitrogen atoms. The undecomposed diazo compound remaining in the areas not exposed to light can then be coupled with a coupling component in the presence of an alkali, while the phenol remaining after light decomposition is incapable of combining with couplers to form azo dye.

At the present time, diazotype reproductions are made by two methods, in each of which a copy sheet is sensitized with a diazonium compound which, upon adjustment of the pH, is capable of reaction with a coupler to form an azo dye.

In the two-component system, there are coated on a support and dried both the light-sensitive diazo compound and a coupling agent, together with various stabilizing substances designed to prevent thermal decomposition of the diazo as well as premature coupling between the diazonium salt and the coupler. The sensitized sheet, under a drawing, tracing, or photographic transparency, is exposed to light of the wavelength and intensity required to destroy or decompose the diazonium compound at the points to which the light penetrates. Development is brought about by treating the paper with ammonia vapor to neutralize the stabilizing acid and to raise the pH to the value at which the coupling takes place. The dye formation is accordingly distributed to form a replica of the original.

In the single-component system, the sensitized sheet contains only the diazonium salt together with stabilizing substances. Following the exposure to light, the image is developed by applying an aqueous alkaline solution of a coupling component. This kind of paper is called semidry or moist paper.

A disadvantage of the diazotype process has been the type of chemical development required for the developing step. The principal objection to the ammonia process for office copy work is the need for a gas chamber in which ammonia vapors can be liberated in sufficient concentration. Machines designed to handle ammonia require the installation of exhaust equipment for removal of the ammonia fumes and are relatively expensive for the occasional use to which they are put. However, gaseous developing treatment offers the advantage that the copy sheet is kept dry throughout the image-reproduction process, thus eliminating the drying step.

Although the moist process gets around the use of ammonia, several other disadvantages are introduced, such as: discoloration of the developing solution on standing, which results in copies of poor quality; time-consuming cleaning of the developing apparatus; difficulties in changing from one color to another; and the need for drying the wet prints. Furthermore, since the dye is formed under wet conditions, it must be wash-fast; for this reason the choice of a suitable diazo and coupler is limited.

Elimination of Aqueous Ammonia

Many efforts have been made in the last 30 years to find another dry developing process for diazotype material which would be free of objectionable limitations, which could be carried out in a simple and expedient manner without expensive equipment or skilled labor, and from which copies of good quality could be economically and efficiently obtained.

To avoid the necessity of handling large quantities of aqueous ammonia, General Aniline and Film Corp.[11] patented the use of a highly concentrated aqueous solution of ammonium carbonate as the alkali in the development of two-component diazotype materials. It is claimed that the operation temperature of the chamber for ammonium carbonate solution is that used for ordinary ammonia. However, the efficiency of development obtained with gases from ammonium carbonate solution is doubtful. Salvadori and Leperche,[12] in a similar proposal, patented development of diazo prints

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* Literature references will be found at the end of this paper.

by a 10% solution of hexamethylenetetramine or triethanolamine in water. Dieterle[13] suggested developing diazotype prints by subjecting them to gases given off by the decomposition of ammonium compounds under the influence of heat. Particularly suitable are compounds of ammonia with weak acids, such as ammonium carbonate or bicarbonate with which it is only necessary to heat the solid carbonate to liberate the gaseous ammonia and bring it into the contact with the exposed surface. In this patent, the water needed for development is provided by the decomposition of the ammonium salt. Other salts mentioned as suitable are ammonium acetate, formate, amino-and imino-sulfate. Recently, Filmsort, a subsidiary of Minnesota Mining and Manufacturing Co., introduced for the development of diazotype microfilm a well-designed unit based on this principle.

Another system, patented by Kalle Co.,[14] utilizes a diazotype paper without the coupling component. After exposure, the paper is subjected, at ordinary or elevated temperature, to the vapor of an aromatic amine such as naphthylamine. While the use of ammonia and the drying operation are avoided here, the process suffers from many other disadvantages, such as the toxicity and the unpleasant odor of the amines, the long developing time, and poor image quality.

Development by Heat

Making use of the fact that the azo-dye formation can be accelerated by heat, several heat developing systems have been proposed. The design of such a system is influenced by the selection of the components and the conflicting properties of the diazonium compounds and the couplers. Since both the diazo compounds and the couplers are intimately mixed in the same layer, it is clear that severe restrictions are placed on the choice of the diazo-couplerpair, if premature coupling is to be avoided. On one hand, the diazonium compound has to be sufficiently unstable to light so that a print can be made at commercial speeds. On the other hand, it must be sufficiently heat stable so that it can be prepared, applied to paper, dried thereon, stored, and exposed, to give clear and sharp prints. Also, the azo-dye formation has to be fast enough to insure good contrast of the image. Taking into consideration these requirements, the following combinations of diazonium salts with couplers are possible:

1. A fast diazo with a fast coupler. This results in an image with very good contrast, but the shelf life of the sensitized sheet is very poor.
2. A slow diazo with a slow coupler. This gives a sensitized material of somewhat improved shelf life. However, at the temperature required for heat coupling, diazo compounds decompose. Since only the undecomposed portion is available for coupling, and, hence, for image formation, the contrast is very poor. Furthermore, slow coupling diazonium compounds also have slow printing speed, which is especially disadvantageous in office copying of letters which are usually written on paper with poor transparency.
3. A slow diazo with a fast coupler. This results in an improved shelf life, but a slow printing speed hinders practical application.
4. A fast diazo with a slow coupler. This gives satisfactory printing speed, but the shelf life of the material and the contrast of the image fall far below commercial requirements.

Other ingredients, such as stabilizers, color improvers, development accelerators, and accelerators for the decomposition of diazonium compounds, when added to the diazo-coupler combination, do not seem to contribute to the quality of heat-developable diazotype papers. The addition of acids to produce unfavorable conditions for coupling does not help much, for the simple reason that the quantity of acid needed to prevent the premature coupling has an adverse effect on the developing speed and contrast of the image. This effect can be partially overcome by the selection of volatile acids. Greig[15] has suggested trichloroacetic acid, which, stable at ordinary temperature, decomposes during the heating period and after decomposition no longer hinders the coupling reaction.

Among many attempts in the past to prevent precoupling was one in which the diazo and coupler were separated by dusting the latter onto a diazo-sensitized paper.[16] The sensitized material, after exposure to light, was developed merely by the application of moisture, either as steam or in some other convenient form. The excess powdered coupler had to be brushed off, obviously a very slow operation. Morecver, the print was of nonuniform dye intensity. Furthermore, under conditions of moderate humidity, precoupling still occurred. A device for steam development was described by Alink and Aninga.[17] Leuch[18] suggested dusting diazo-sensitized paper with a mixture of phloroglucinol, sodium benzoate, and starch. After exposure, the paper is developed in a 10% solution of sodium carbonate. It has also been proposed to coat the diazonium compound and the coupler solution on opposite sides of a sheet of paper. This procedure, like all others described in this group, does not prevent precoupling, since the two ingredients ultimately diffuse and migrate until they are intermingled.

As can be seen, the process of developing diazotype papers by heat may be simple in theory, but the actual practice is much less simple and, until now, chemists have had difficulties in finding an acceptable solution to the problem.

Developing Agent in the Sensitized Layer

To simplify the chemical development of diazotype paper, it has been repeatedly proposed that developing agents be incorporated in the sensitized stratum itself, but in such a condition that they do not cause development until heated or steamed. In one such effort, a dry nonvolatile alkaline salt was dusted on the print, and development was started by applying moisture or steam. Development resulted from the direct contact of the particles of the alkaline salt with the paper in the presence of moisture, and thus, for the process to work satisfactorily, the alkaline salt had to be very evenly and finely distributed over the entire surface of the paper. This procedure required a relatively long time for development, demanded apparatus for maintaining an atmosphere of steam or vapor, and could cause the lines of the final print to bleed or spread.

Another approach to the problem was made by Neugebauer and Süs,[19] who suggested producing the alkali necessary for the development at the moment of development by chemical conversion of several substances which, individually, are not capable of producing alkali. The substances are, in general, neutral or even acid. The reaction takes place in the presence of water which is applied to the material to be developed as either steam or liquid. As an example, the patent mentions a mixture of basic aluminum acetate and sodium fluoride; during the reac-

tion, complex sodium aluminum fluoride is produced and sodium hydroxide is set free. Sodium fluoride can be replaced by other alkali fluoride or other suitable substances forming complexes, e.g., sodium or potassium oxalate. Also, alkali salts of citric or adipic acid can be employed. Substitutes for the aluminum acetate may be other basic salts of aluminum or other metals, such as zinc, lead, or zirconium, or corresponding hydroxides.

For thorough fast development, Morrison[20] recommended that there be added to the sensitizing solution chemicals that decompose in the vicinity of the developing temperature and thereby release ammonia. The best choice for this purpose seems to be urea; it is very soluble in water, its reaction is neutral, it does not change the pH of the sensitizing solution to a marked degree, and its melting point is 133°C, which is in the favorable range. The recommended quantity of urea to be added is about 6–7 grams/100 cc of sensitizing solution. The speed of development and the intensity of the image is, however, dependent on the acidity of the solution.

In addition to urea and substituted ureas, thiourea and its substituted derivatives are claimed in a recent French patent.[21] Other compounds that have been investigated include urea derivatives (e.g., guanidine and biuret) and a series of ammonium salts of organic and inorganic acids. Amino acids, such as glycine or imino-acetic acid, did not yield any useful results.

Van der Grinten's formulation[22] also belongs to this class. For sensitizing heat-developing diazo paper, he uses a solution of 5% dimethylamino-3,5-xylol-4-diazonium chlorostannate, 0.5% phloroglucinol, 3% sodium acetate or some other salt of a strong alkali, and a weak, volatile acid that decomposes at elevated temperature, such as potassium malonate or potassium succinate.

Although such techniques can be made to operate, they have been found unsatisfactory in that the useful storage life of the sensitized stratum is severely shortened; color formation takes place gradually even without the application of heat or steam. As a result, if such processes are used, it is necessary to make sure the sensitized material is relatively fresh; in many cases, even a few weeks' storage is too long.

Separate Developing Sheets

Another method for the development of diazotype papers uses separate developing sheets impregnated with a composition containing one compound or a combination of compounds, which, upon exposure to heat even for a very short time, liberates the vapor of an alkali or a coupler. Such a developing sheet may be brought into intimate contact with the coated side of the diazo sheet, e.g., by passing the two sheets together between heated rollers, and thus the developing medium is made immediately available.

The suggestion of Marron and Shoemaker,[23] which belongs in the same category, utilizes a chromium hexamino compound such as chloride; of course, any ammonium compound giving off ammonia by heat decomposition will produce the same results. Again, especially suitable for this purpose are compounds of ammonia with weak acids or organic compounds, such as ureas and thioureas. The heat applied has to be sufficient to liberate a small amount of ammonia from the developing sheet. The amount of ammonia necessary to effect the desired pH adjustment for the coupling reaction is only a small proportion of the available ammonia in the developing sheet, so that, theoretically, the developing sheet may be used over and over again.

Greig[24] incorporated urea and the sodium salt of a weak acid in high-molecular-weight polyethylene glycol and coated the mixture on a support. This developing member is heated to the melting point and brought into contact with the exposed diazo sheet; the alkali necessary for development is transferred, causing the color reaction. When the coupler is also added to the developing sheet, the sensitized paper contains only the diazo component, improving the shelf life considerably. In this last method, which in a way resembles the semiwet process, the speed of the coupling reaction is proportional to the developing temperature. At higher temperatures, near the melting point of the vehicle, however, offset occurs, and the waxy material is transferred to the diazo paper, while some of the diazonium compound is absorbed by the developing sheet. Consequently, the developing sheet cannot be reused, and the appearance of the print may be poor. An improvement seem : to be achieved by impregnating a fibrous absorbent carrier with a coupler capable of thermal transfer or vapor distillation. The binder is thus not necessary, and the transfer of the chemicals to the opposite sheet is eliminated.

To secure a rapid reaction, Benbrook and Herrick[25] suggested using a fast diazo, such as 4-benzoylamido-2,5-diethoxybenzenediazonium chloride. Separate developing sheets would be especially advantageous for office copy work, because of the elimination of expensive and complicated equipment and chemicals. An entirely dry process, it makes use of but two sheets of paper — one containing the latent image in the form of undecomposed diazo compound and coupling component, and the other containing a compound which releases an alkalizing medium at elevated temperature. The two-sheet process somewhat resembles the diffusion transfer process, very much used at present in office copying.

Multilayer Coatings

In spite of the many advantages of the two-sheet process for office copying, the separate developing sheet seems to be objectionable from the commercial point of view. Logically, efforts were made to apply to a single support the active components in isolated layers, separated by a layer of a material which melts at temperature below the decomposition temperature of the diazonium compound. Water-soluble resins, or resins soluble in the same solvents in which the diazo compound and/or the coupler are soluble, are worthless, because they dissolve one of the components and leave it on the surface. Also, where use is made of resins or polymers and their solvents that do not attack the active components, the coating is mostly unsuccessful. Where the coating is too thin, the film formed after drying is not continuous and allows contact between the diazo and the coupler. When the coating is made heavier, the film does prevent contact between these two compounds, but development at the proper time is incomplete or does not take place at all. Suspension of the components in a resin solution is also unsuccessful. In this case, the light sensitivity of diazonium compounds is dependent to a certain degree on the particle size of the diazonium salt.

Multilayer coating using polyethylene glycol as an intermediate layer was proposed by Kendall and Reynolds.[26] Their patent is based on the fact that, when heat rays or infrared radiation is passed through a sheet of material carrying an image in printer's ink, carbon black, or silver, the radiation is absorbed by the image but is transmitted more freely by the nonimage areas.

The same principle was successfuly used by Minnesota Mining and Manufacturing Co. in their Thermo-

Fax copying process. The diazotype material, as defined, is placed in contact with an image sheet and the assembly subjected to heat or infrared radiation; as a result, the diazo material is heated locally, in those areas that are in register with the image areas. The interlayer of fusible material melts in those same areas, and the diazo compound and azo-coupling component in those areas can now interact to form an azo dye. Since the radiation source is substantially free of short wavelengths, it is necessary to destroy the diazo in the nonimage areas by exposing it to daylight or ultraviolet radiation. If the exposure source includes both heat and ultraviolet radiation, it follows that in the image areas the azo dye will be formed, while in the nonimage areas the diazonium salt will be destroyed. The resulting copy is then light and heat stable. When the diazo compound has a high degree of heat stability, the exposure may exclude light which would destroy the diazo compound in the nonimage areas. The residual diazo may then be used to obtain, by means of light exposure, a second image which may be developed with an azo-coupling component; this superimposes on the primary image a secondary image in a different color.

Self-Developing Diazotype Paper

If the diazo compounds, either in solution or as solid substances, are exposed to light, they decompose into a phenol and nitrogen. If the phenol is very inactive, it will not couple with the remaining undecomposed diazo compound. The undecomposed diazo is then coupled with whatever coupling component is present, by treatment with an alkali solution or by exposure to ammonia vapor. However, if the product of photolysis is reactive, it reacts spontaneously with the undecomposed diazo and obviously a negative print is obtained. This mechanism formed the basis of the early negative diazotype process: the procedures of West,[27] Feer,[28] and Andressen[29] are typical. In the Andressen process, for example, the sensitized paper was placed under a drawing and exposed to light until about half the diazonium salt was decomposed in the exposed areas. The paper was then washed in a weak ammonia solution, producing a reaction between the phenol and the nonphotolyzed part of the diazo compound, and a negative print resulted. Fixing was achieved by rinsing with water or by a second exposure to light to decompose the remaining diazo.

An improved method for obtaining negative prints was realized by the introduction of "self-developing" layers.[20,21] In self-developing layers, an azo dye is formed by the union of the photolysis product remaining in the layer with the available excess of diazonium salt still present in the layer, without the addition of any further reagent. Thus we may say that the self-developing papers are based on the autocoupling properties of certain diazo compounds in connection with their photolysis products. In this process, exposure under a drawing to slightly actinic light partially decomposes the diazo compound in the places touched by the light; a phenol is formed, which couples spontaneously with the nonphotolyzed part of the diazo, and the part of the print not protected by the drawing assumes a deeper color. A second exposure to a strongly actinic light, without the drawing, entirely destroys the diazo that has so far been protected, and the outline appears in white on a dark background. A negative is thus obtained from a positive.

Humidity helps this reaction, and it is therefore helpful to dampen the paper with water between exposures, or to incorporate into the sensitizing solution hygroscopic agents, such as glycerin or glycols. The autocoupling reaction can further be accelerated by heating the copy after the exposure, especially when urea is present in the coating.

Light-sensitive materials that can be used for this purpose include benzene diazonium compounds[31] which readily hydrolyze to form an unstable diazonium hydroxide and which couple with their photolysis products to form a dye at a considerably faster speed than they couple with the hydroxide. According to DeBoer and Klaassens,[32] naphthalene diazonium compounds give a material of greater stability than can be obtained with benzene diazonium compounds.

In the Frangialli process,[33,34] when a strong actinic light is used for exposure and the resulting print, with tracing withdrawn, is exposed to light that is only slightly actinic, the outline of the drawing becomes colored, either spontaneously or after remaining in the dark for a few seconds. If a pencil drawing is used, where the line is only slightly opaque and allows part of the light to pass through, a single strongly actinic exposure is sufficient. In this manner, a direct image in colored lines is obtained on a white background, and the copy is definitely fixed.

A similar method, based, however, on quite a different principle, was patented by Philips.[35,36] Instead of utilizing the coupling properties of diazonium compounds, this process is based on the oxidative properties of certain diazos and on the formation of colored oxidation products from the products of the photolysis of these or other diazonium compounds. On exposure, the suitable diazonium compound forms primarily a phenol, so substituted in the benzene nucleus that the phenol can be oxidized by the diazonium compound itself or by another diazonium compound also present in the layer to form a colored compound. Suitable diazonium compounds include those having, in the benzene nucleus, at least one OH-group ortho or para to the diazonium group. In some cases this OH-group may be replaced by an NH_2-group, which, on exposure, produces a readily oxidizable aminophenol. One of the hydrogen atoms of the amino group may be further replaced in some cases, by an alkyl-, an aryl-, an aralkyl- or a naphthyl-group. For instance, *p*-hydroxybenzenediazonium chloride upon exposure decomposes into hydroquinone, nitrogen, and hydrochloric acid. If the exposure is such that not all the diazonium compound present is converted into hydroquinone, the hydroquinone is oxidized by the remaining diazonium compound to form a colored oxidation product. This oxidation can, of course, be considerably accelerated by moderate heating.

At first, the self-developing process seems simple enough to solve the problems of chemical development of diazotype papers, but it is more complicated in practice than in theory. The formulator of self-developing layers has to realize that there is a close connection between the pH of the layer and the formation of the dye. Furthermore, to produce the desired results, the selected diazonium compound must decompose in less time than it takes for the dye to form. Also, the amount of actinic light used for exposure, the pH value of the light-sensitive layer, and the moisture content of the layer must be in proper relationship, and what the proper relationship is depends upon the specific diazonium compound used. To assure the maximum intensity of the image, it is also necessary to regulate the intensity of the light source so that the ratio of the phenol produced to the residual diazo forms the theoretical molecular ratio. To meet all these requirements is very difficult and commercially next to impossible.

Diazo Sulfonates

Up to this point, we have been discussing the use of diazonium compounds capable of coupling with azo components. However, if these compounds are reacted with sulfites, there result diazo sulfonates which cannot couple, and hence will not form azo dyes. But if the diazo sulfonates are decomposed by heat, which disengages the diazo compound contained in the diazo sulfonate, the diazo then couples with the coupler and forms a positive azo dye image in all areas not struck by the light. With the help of a light-sensitive material of this type, copies can be produced without the use of alkaline solutions or gases for development.

In this process, the material, which consists of paper, film, or another suitable support carrying a light-sensitive diazo sulfonate together with a coupling component, is first exposed to light under a pattern, and thus in the exposed parts the diazo sulfonate is destroyed. Next, the print is heated sufficiently to form a dye in the unexposed parts. It is necessary to use aromatic diazo N-sulfonates that have only a moderate velocity of coupling, but a high sensitivity to light. Furthermore, in designing the formulation, care must be taken that the coupling diazo compound produced as an intermediate product in the decomposition of the diazo sulfonates by light has no opportunity to couple with the azo component present in the material, since this would lead to an undesirable background discoloration. Süs[37] uses diazo sulfonates which are derived from *p*-aminodiazo compounds of the benzene series, wherein either one or both hydrogens of the amino group are substituted by an alkyl group. The N-sulfonates of dialkylaminobenzene diazo compounds are preferred.

The light-sensitive layers coated in accordance with this invention do not have as long a shelf life as desired. Although this instability can be overcome by adding to the sensitized solution a small amount of sodium bisulfite, together with ketones, ketonic acids, aromatic aldehydes or their substitution products,[38] which will form addition products with the bisulfite, at the same time the photosensitivity of the layers will be lowered. Both the stability and the light sensitivity of such layers can be improved to a higher degree by the addition of water-soluble salts of aromatic sulfonic acids of the benzene and naphthalene series,[39] which are substituted by halogen or alkyl or alkoxy groups para to the sulfonic group (1-ethoxybenzene-4-sulfonic acid). Because the photosensitivity of the layer bears a direct relationship to the concentration of the sulfonic acid salt, salts with greater solubility in water are more effective.

Material of this type can be used to form an image by selectively heating only predetermined areas.[40] For example, this technique can be used to trace the moving indicator of a recording instrument or to record motions induced by long-distance transmission.

In comparison with standard diazotype papers, light-sensitive materials prepared from aromatic diazo N-sulfonate have the disadvantages of being less stable when stored in the unexposed state and of having insufficient photosensitivity. Thus this type of diazotype material cannot yet be introduced for practical use.

Conclusions

The main reason for the failure of efforts to put heat-developable diazo paper on the market is the fact that the compounds used as the source of the alkalizing medium decompose or react slowly, even at normal temperature, producing the coupling reaction prematurely. To solve this problem, we need chemicals which are very stable at all temperatures up to the point of decomposition. Heated to this point, these compounds should decompose rapidly and completely, liberating the alkali at a sufficient rate to cause rapid development. Similar properties must be required of diazo sulfonates, to improve the keeping quality of papers sensitized with them. Of course, light sensitivity, also, should be kept in mind. For future developments, probably the most attractive are experiments with unreactive couplers which are activated by heat to couple with a diazonium salt. Multilayer coatings have been, with one exception, neglected. In the same manner in which Thermo-Fax produces its image by rapid reaction of two compounds in the melted or softened state, it may be possible to prepare similar material based on the diazo principle. The need for moisture may complicate the problem.

Although, at present, hope for the development of an acceptable heat-developable diazo material seems very small, such a goal is not unachievable.

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• Book and Journal Reviews

Books Received

Press Photography

ROBERT B. RHODE AND FLOYD H. MCCALL, Macmillan, New York, 1961, xi + 244 pp., $6.00

The authors, one an associate professor of journalism at the University of Colorado and the other Chief of the Photographic Department of the *Denver Post*, wrote this book as a working guide for the press photographer who is already familiar with the fundamentals of reporting and picture taking. Subjects covered include the choice and operation of the camera, use of lenses, filters, *f*-stops, and shutter speeds, lighting techniques, composition and editing, choice of film and printing papers, and new developments in the news-photography field such as ROP color, the trend to small reflex-type cameras, and fast developing and printing processes. A brief history of photography as related to press reproduction is included.

Odhams Manual of Photography, The Practical Guide for Amateurs

Macmillan, New York, 1961, 353 pp., $7.50

This book, originally published by Odhams Press Ltd. in 1960, is the combined work of 14 authors. It includes chapters on equipment, processing, color, stereoscopic photography, cinematography, and homemade gadgets, and has separate chapters on special aspects of photographing people, animals, landscapes, buildings, and interiors. The book is well produced and well illustrated, and should prove useful for both the beginner and the more advanced amateur.

Supplementary Electron Microscopical Observations of the Process of Sensitization of Photographic Emulsions

T. HIBI AND K. YADA, *Electron Microscopy* (Japan) **8:** No. 2-3: 181–83 (1959) (in Japanese)

A method has been worked out for the electron microscopical observation of the physical-chemical and photochemical changes in emulsion grains at different stages of chemical sensitization, photolysis, or development, not incurring the destruction of the grains and therefore suitable for multiple or even continuous observation of the same crystals. The method is based on obtaining multiple replicas which then form the subject of study. A description is given (without illustrations) of some results obtained with the aid of this method on photographic emulsion layers of process-type plates. Photolysis was studied at different levels of exposure corresponding to the latent image and to direct print-out. The formation of silver particles was observed, some of them being inside the grains; in the latter stages of photolysis (with exposures to sunlight of up to 1 hr), the concentration of silver was observed in the form of one or two coarse centers on each crystal. Under these conditions there took place a considerable change in the form of the grains, including their separation into two halves and the formation of layers. Observation of the slow development of the same grains in a weak developer (D-72 at a dilution of 1:20) showed the presence of sharp steps in the course of the development. The instantaneous changes of rate of development were connected with the degree of imperfection of the grains, both on the surface and also (according to the degree of solution) in depth. — *S. C. Goddard (translated from Referativnyi Zhur, Fiz.)*

The Perception of Reproduction Colors in Color Television

ICHIRO SŌMA, *Studies of Color* (Japan Color Research Institute), **7:** No. 2: 29–37 (1960) (in Japanese)

The author studied the fidelity of color reproduction in color television by successive color matching. He found that (a) light and dark colors were poorly reproduced, (b) significant hue shifts occurred mostly in the blue and green directions, and (c), in general, highly saturated colors were reproduced at significantly lower saturations. The gamut of chromaticities corresponding to color names and memory-colors for eight familiar objects were determined; the reproduced colors tended to be within these limits. Further work is being conducted but the author's tentative findings are that the first requisite for color television reproduction is that it should produce an impression of "naturalness" rather than strictly reproduce the original chromaticities. — *C. J. Bartleson*

New Developments in the Field of Apparatus for High-Speed Photography and Cinematography

A. A. SAKHAROV, *Tekh. Kino. i Televideniya*, 4:63–68 (December 1960) (in Russian)

Recent apparatus made in the Soviet Union for high-speed photography and cinematography is described.

The CR-16 sensitometer, made by the State Optical Institute covers a wide spectral range and is made to give characteristics of photographic materials with exposures of from 6×10^{-3} down to 10^{-7} sec. The temperature of the photographic material can be varied from $-150°$ to 60°C.

A prototype high-speed camera with discontinuous film transport (also made by the State Optical Institute) works at up to 1,000 frames/sec. It uses 35mm film but the principle should be successful with other formats. The film is braked at a high frequency by means of a pulsating pressure element at the gate, the slack film being allowed to form a loop before the gate at each stoppage. The perforations are engaged only by teeth on continuously rotating sprocket drums.

Described are three "waiting" cameras, i.e., cameras in which the mechanism is allowed to operate at full speed while waiting for the event which trips the shutter. The cameras are: the SSKS-3, made by the Leningrad Institute of Fine Mechanics and Optics, a multiple-objective rotating-beam camera taking up to 800 frames at a

speed of 500,000/sec; the ZhLV, made by the Institute of Physical Chemistry of the Academy of Sciences, which achieves frame speeds of 20,000–3,000,000/sec by means of a rotating mirror system; and the RKS-11, made by the Leningrad Institute of Motion Picture Engineers, a moving-grid camera operating at 1,000–100,000 frames/sec.

Lenticular grids made by NIKFI are claimed to pass more light than those used in the Sultanoff camera (U.S.A.) and to have a finer structure than the Courtney-Pratt camera (England). The characteristics of the grids are tabulated.

Other apparatus very briefly described includes viewing apparatus for analyzing high-speed films. — *S. C. Goddard*

Primary Color Separation and Inter-Image Effects in Development of Color Photographic Materials

D. K. Balabukha and N. V. Makova, *Tekh. Kino. i Televideniya*, **4**:31-40 (December 1960) (in Russian)

The term "primary color separation" means the initial analysis into the three color records carried out at the moment of exposure to the subject. Its efficiency cannot be properly evaluated without reference to the final synthesis. A mathematical analysis of color separation due to Nyuberg (*Uspekhi Nauch. Fotografii, 2:* 134 (1954)) is outlined and the derivation of his color-separation zones is explained. The method is then used to show that the interimage effects of a multilayer color negative are equivalent to automatic color masking. It then appears that the efficiency of color separation of the multilayer negative material is greater when the final color image is synthesized by an imbibition positive process than when a multilayer positive material is used. — *S. C. Goddard*

Uspekhi Nauchnoĭ Fotografii, Akademiya Nauk SSSR

Volume 7, 1960 (in Russian)

Résumés by S. C. Goddard

The Nature and Production of Photographic Sensitivity (with Regard to the Theory of Mitchell)

K. V. Chibisov, pp. 1-24; cf. *J. Phot. Sci.*, **7**:41-54 (1959)

A summary is given of the ideas of Mitchell and his collaborators on photographic sensitivity and the formation of the latent image. The considerable amount of work done in the USSR on the effect of ripening conditions on digestion kinetics, and on factors in emulsion-making which affect distribution of the surface and internal image is summarized. Evidence for the presence of complex-forming impurities in gelatin is reviewed. It is concluded that silver is formed during ripening as well as during digestion, and becomes situated on local defects in the crystalline silver bromide lattice. A pure, unsensitized silver bromide emulsion grain is an abstraction. The work of Kirillov and others on the fine structure of the absorption spectrum of silver bromide, and the changes brought about in it by the presence of impurity centers and latent image, it reviewed and accepted as valid. Mitchell's views on the importance of local defects in the crystalline lattice of the silver bromide grains are regarded as well supported by the evidence, although a warning is given that deductions made from the behavior of large silver bromide crystals prepared from the melt will not necessarily hold for small emulsion grains. In particular it is considered that the results of experiments on practical emulsion making show that Mitchell's ideas on the surface distribution of the products of chemical sensitization are incorrect and that internal centers play a much greater part than he imagines. The maximum speed attainable during digestion is in fact determined by the substructure of the emulsion grains which is a result of the ripening conditions. Doubts are cast on Mitchell's insistence on the importance of silver sulfide as the active product of chemical sensitization. Finally, unlike Mitchell, the author believes that silver centers are present in the emulsion grain before exposure, and therefore he alters the course of events as prescribed in the Mitchell hypothesis to accommodate this fact. This leads to the formation of latent-image centers larger in size than those postulated by Mitchell (58 refs.).

Processes of Aging and Stabilization of Photographic Materials

V. I. Sheberstov, pp. 25–49

A review of the subject is given, based on articles ranging from the work of Carroll and Hubbard in 1931 to the latest work of Sheberstov and his collaborators (76 refs.).

The Aging of Photographic Emulsions and the Intensity of Light Exposure

S. M. Solov'ev and V. A. Dmitrieva, pp. 50–56

Experiments with silver bromide sols and experimental photographic layers are described which show that the effect of aging varies according to the exposure required to give the density used as a criterion. With a higher level of illumination the effect of aging is to give less developed density, while with low intensities an increase in density is observed.

The Influence of the Conditions of Making and the Processing of Photographic Layers on Reciprocity Failure

K. V. Vendrovskiĭ, pp. 57–76

A literature review with 129 references.

The Influence of Chemical Sensitization on the Speed of Photographic Emulsions at Low Light Intensities

Yu. Sh. Meshkovskiĭ, pp. 77–86

The work was carried out with an experimental silver iodobromide emulsion made by centrifuging, with subsequent dispersion of the silver halide grains in water, so as to eliminate the gelatin to a large extent. In this form they were digested after the introduction of hydrazine sulfate, sodium thiosulfate, gold thiocyanate, or sodium nitrite (the last as a bromine acceptor). With thiosulfate sensitization the shape of the sensitometric curves for different times of exposure remains unaltered but the curves are displaced towards the right as the time of exposure is increased. With hydrazine sensitization the sensitometric curves differ in shape as the time of exposure is altered, the contrast increasing with the longer times of exposure. The presence of hydrazine in the emulsion therefore reduces the low-intensity reciprocity failure to a marked extent. At the same time the minimum of the reciprocity failure

curve is displaced towards the longer exposures. Gold sensitization does not give an increase in speed at low intensities and hence increases low-intensity reciprocity failure. Sodium nitrite in the emulsion showed no effect on reciprocity failure. The difference in the action of sodium thiosulfate and hydrazine is thought to be due to the formation of two different kinds of silver centers.

The Rôle of Thiocyanate Ions in the Chemical Sensitization of Photographic Emulsions by Gold

I. R. Protas, Yu. A. Krakau, and P. T. Sidorenkova, pp. 87–95

An investigation has been made into the interaction between silver bromide and ammonium thiocyanate under conditions close to those obtaining in emulsion making. It is shown that the ratio between the equilibrium concentrations of bromide ion and thiocyanate ion in solution corresponds to the ratio of the solubility products of silver bromide and silver thiocyanate derived from the law of mass action.

No interaction is possible between silver bromide and thiocyanate ion at concentrations of thiocyanate ion which are usual in the sensitization of emulsions by means of the complex salt $NH_4Au(CNS)_2$. It was shown that on the introduction of thiocyanate ion in larger concentrations than those taken in practice, there was some correspondence between the quantity of thiocyanate ions taking part in the exchange reaction with silver bromide and the increase in sensitivity of the layer. Full parallelism between the two processes was not observed, however. The presence of thiocyanate ion in concentrations of 0.00255 to 0.0262 *M*, with prolonged digestion of the emulsion, did not entail an increase in the dimensions of the silver halide grains.

The theory is put forward that, on sensitization of an emulsion with gold, the part played by the thiocyanate ion consists in controlling the rate of decomposition of the complex gold ion to the metal and in reducing functions, but not in its action as a silver bromide solvent.

A Study of the Influence of Sodium Thiosulfate on the Photographic Properties of Emulsions Sensitized with Gold

I. A. Novikov and N. S. Gafurova, pp. 96–102

The maximum speed to light of emulsions containing only small quantities of natural sensitizers and gold passes through an optimum as the sodium thiosulfate concentration is increased. In the presence of larger quantities of natural accelerators or gold the action of thiosulfate is insignificant. Sodium thiosulfate does not destroy the specific pattern of the change in the photographic properties during digestion caused by gold. The gamma of emulsions containing very little natural sensitizer and gold was increased somewhat in the presence of sodium thiosulfate, while the gamma of emulsions made with the usual gelatins or the usual quantities of gold was not altered.

An attempt has been made to explain the observed relations by the change in photographic activity of gold impurity centers when silver from digestion is included in their composition. (*Based on authors' abstract*)

Changes in Dispersion of Fine-Grain Emulsions During Digestion

I. A. Novikov, pp. 103–108

It has been found that during the digestion of fine-grain emulsions marked changes may occur in their dispersity. The enlargement of the emulsion grains during digestion is greater with increase in the initial dispersity of the emulsion, with increase in the pH of the medium, with increase in temperature of digestion, and with decrease in the pBr of the emulsion and of its content of the stabilizer 5-methyl-7-hydroxy-2,3,4-triazoindolizene. The possibility is discussed of the observed change in dispersity during chemical sensitization of the emulsions influencing their photographic properties and the kinetics of digestion. (*Based on author's abstract*)

Continuous Processes of Photographic Emulsion Making

N. I. Kirillov, Yu. G. Chikishev, and V. Zelikman, pp. 109–114

After a brief mathematical analysis of the conditions obtaining in continuous emulsion making, the various stages are considered from the point of view of the previous suggestions for their continuous operation. Finally, two schemes for the continuous operation of the whole emulsion-making process are suggested, one involving separation into different grain-size classes between the ripening and digestion, and the other with the separation following digestion. Flow sheets are given for both schemes.

Gelatin Concentration in Physical Ripening

V. L. Zelikman and E. B. Kondrat'eva, pp. 115–119

Experiments were carried out with two ammoniacal silver bromide emulsions: a fine-grain lantern-slide type with a mean grain size of 0.07μ^2 and a coarse-grained negative type with a mean grain size of 2.12μ^2. As the gelatin concentration is decreased, the speed passes through a maximum (at about 0.025% for the fine-grain and about 0.2% for the coarse-grain emulsion), fog rises slightly and the gamma of the fine-grain emulsion falls slightly until the gelatin concentration reaches 0.1%, after which the rise in fog and the fall in gamma both proceed much more rapidly, probably owing to aggregation of the emulsion grains. No direct connection could be found between the concentration below which aggregation occurred and the specific surface of the grains. The effects apparently are not due to the different conditions of sedimentation at different concentrations of gelatin, since allowing the emulsions to stand had no effect on their aggregation.

Modern Ideas on the Structure of Gelatin

S. M. Levi, pp. 120–133

A literature survey with 68 references covers advances in gelatin research made chiefly during the last ten years.

Protein-Like Impurities in Photographic Gelatin

E. A. Zimkin and S. I. Paronik, pp. 134–136

A protein-like substance containing 3.9% cystine and 1.2% tryptophane was separated from photographic gelatin. It is suggested that it is a residue of the proteins accompanying collagen. The cystine of the noncollagen protein may be the source of labile sulfur in the gelatin. The better kinds of photographic gelatin should be free from noncollagen proteins. (*Translation of authors' abstract*)

Modern Ideas on the Rheological Properties of Gelatin Solutions and Photographic Emulsions

S. M. LEVI, pp. 137–149

The rheological properties of gelatin are discussed on the basis of existing literature, and data are tabulated and plotted to show the rheological properties of gelatin and emulsions with and without color couplers. A number of factors which affect the rheological properties of gelatin and emulsions are then considered, including the presence of surface-active agents (in particular color couplers), molecular weight, temperature, gelatin, age, and silver content.

A Search for Methods of Improving the Structural and Mechanical Properties of Photographic Materials for Nuclear Research

V. M. UVAROVA AND V. A. MYL'TSEVA, pp. 150–160

The fundamental reason for the distortion of the light-sensitive layer of a photographic material (the authors are particularly concerned with the distortion of tracks in nuclear emulsions) is the instability of the molecular structure of the emulsion vehicle. A stable material should be in equilibrium, i.e., its potential energy should be a minimum and there should be no residual internal stresses. Neither hardening of the emulsion nor the introduction of hygroscopic substances give rise to the required equilibrium. The preferred methods of stabilizing the mechanical properties of a layer are annealing by keeping the layer at a high temperature for a length of time, and substitution of part of the gelatin by compounds with high molecular weight.

Methods of Hardening Photographic Emulsions

V. L. ZELIKMAN, pp. 161–169

The literature is reviewed and 64 references are given.

The Action of Mixed Wetting Agents in Multilayer Coatings

S. M. LEVI, pp. 170–177

A distinction is made between "downward" and "upward" wetting action: the downward action being directed towards the substrate on which the layer is being coated and the upward action being directed towards a subsequent coating. Mixtures containing salts of alkenylsuccinic acids and polyglycol ethers were examined for a number of wetting properties and the results are tabulated.

In general, it is concluded that the properties of the components in mixtures of wetting agents are additive. Thus the lowering of surface tension produced by a mixture of wetting agents is a mean value for all the components. If a property depends on one component only, then that property is completely preserved in a mixture containing that component. The results show that it is possible to obtain a given complex of properties by a suitable mixture of wetting agents.

The Elementary Composition of Nuclear Photographic Emulsions

M. F. RODICHEVA, pp. 178–182

Elementary analyses of NIKFI Type-R emulsions (conditioned at 58% RH) are tabulated. The silver halide was determined by the method of Swinnerton and Waller, and the gelatin phase was analyzed by a method due to M. O. Korshun, in which the gelatin is not oxidized directly but is first subjected to pyrolysis. A comparison is made between the elementary compositions of NIKFI Type-R emulsions and Ilford G-5.

A Study of the Concentration Effect in the Optical Sensitization of Photographic Emulsions

A. V. BORIN, pp. 183–190

The effects produced by changes in the concentration of three thiacarbocyanine sensitizing dyes in an ammoniacal iodobromide emulsion have been studied. In general, as the concentration was increased, the natural sensitivity of the emulsion fell in a step-wise fashion. Experiments described show that the fall in sensitivity is due to an actual desensitization rather than to a screening effect of the dye. Photolytic bromine is thought to be prevented by the adsorbed layer of dye from combining with the gelatin, and hence remains available for rebromination of the silver atoms.

A Study of the Interaction Between Merocyanines and Silver Ions in Solution

K. I. POKROVSKAYA, pp. 191–200

Certain merocyanine dyes which are not in the form of salts easily form unstable complexes with silver ions. This reaction has been studied for a large group of merocyanines differentiated by the nature of the carbonyl-containing and heterocyclic nuclei and by the length of the polymethine chain.

It is shown that, of the merocyanines studied, those especially prone to silver complex formation were the most basic derivatives of thionapthen-3-one, followed by dyes with coumaran-3-one and 3-ethylrhodanine residues. The least basic derivatives of indan-1,3-dione did not in general enter into reaction with silver ions.

In each of the series of merocyanines mentioned, the ability to form silver complexes and the fogging action on photographic emulsions grow with increase in the basicity of the nitrogen-containing heterocyclic residue and with lengthening of the polymethine chain. (*Translation of author's abstract*)

Hypersensitization of Infrared Materials

S. M. SOLOV'EV, pp. 201–209

The following formula has been worked out for hypersensitizing infrared photographic materials:

Silver nitrate, 1% soln.	1.5 ml
Ammonia (d = 0.910)	0.75 ml
Water to make	100 ml

Plates or films are treated in this bath for 4 min, rinsed for 5 sec in distilled water, bathed for 10 sec in a 1:1 aqueous-alcohol bath, and rapidly dried.

Tests were carried out on a number of published formulae. The best results were shown by a Gevaert formula, but for an equally good photographic performance it was not so convenient as the author's formula (above). Experiments on hypersensitization of infrared materials in mercury vapor showed either no or negligibly little influence on photographic properties. (*Translation of author's abstract*)

Means of Increasing the Stability of Hypersensitized Infrared Films

S. M. Solov'ev and N. M. Parfenova, pp. 210–218

5-Methyl-7-hydroxy-2,3,4-triazaindolizine will effectively stabilize infrared films hypersensitized by means of the bath described by S. M. Solov'ev (*preceding abstract*). Treatment remains effective for 20-22 days, after which fog begins to grow and there is some lowering of the effective speed. The film after hypersensitization, as in the above-mentioned paper, is rinsed in water for 1 min and then treated for 4 min in a bath consisting of from 5-8 ml (depending on the degree of fogging of the film) of 1% aqueous solution of stabilizer diluted to 1000 ml. with water. The film is then rinsed in 70% alcohol and quickly dried.

A Study of Local Effects in Development and Their Influence on the Quality of the Motion-Picture Image

Yu. I. Bukin, pp. 219–229

Local development effects have been studied in repeated intermediate printing (up to ten times), the printings being carried out so as to keep two reference densities (a black and a white) constant. The increase in grain was shown to be due to an increase in the contrast between the grains and the background due to local development effects. A distortion of the gradation was produced, the intermediate densities tending to approximate to the reference densities, so producing a stepped curve with the disappearance of intermediate tones. Fine-grain films show the effects less, a larger number of repetitions being required to give the same degree of distortion, although dry collodion layers gave very poor results.

The effects were worsened when development was carried out without agitation, but greater agitation than the normal showed no improvement. The composition of the developer solutions was without effect except in the case of a tanning developer based on pyrogallol in which the local effects were enhanced.

Bromide streaks were studied by means of "effectograms" in which square patches of density were superimposed on a continuous density wedge. The effectograms were developed in a vertical position so as to allow formation of bromide streaks under the patches. ΔD, the difference between the density of the background with and without the bromide streak, was plotted against γ. The greatest ΔD found was produced by hydroquinone with caustic alkali, giving a very large fog. The quantity of potassium bromide in the developer had little influence on the effect in amidol and in hydroquinone with sodium carbonate, but had a strong influence in hydroquinone with caustic alkali, which gives a very high fog without potassium bromide and less when the bromide is present. The effect is ascribed to the slowing down of development by the bromide and not to solution of the silver halide.

A Study of the Stability of the Working Bleaching Solutions Used in the NIKFI Process

N. I. Kirillov, A. M. Voĭtsekhovskaya, and N. E. Kirillova, pp. 230–235

A bleach bath containing potassium ferricyanide and sodium thiosulfate is used in the NIKFI process for processing multilayer color films (*Uspekhi Nauch. Fotografii*, **4**: 269 (1955)). Experiments have been carried out on the chemical reactions occurring during storage of the bleaching solution and it has been shown possible to increase the stability by adding ammonia or potassium carbonate. Buffered bleaching solutions and the use of counter-current bleaching of color films are also recommended.

The Use of Different Fixing Solutions in the NIKFI Process

N. I. Kirillov, A. M. Voĭtsekhovskaya, and N. E. Kirillova, pp. 236–239

A number of weakly-acid fixing baths have been studied for their suitability in the NIKFI process for the processing of multilayer color film. A wide choice of fixing solutions is available. The acid content, depending on the content of sulfite and the acidifying substance used, may vary within wide limits provided that the pH is kept constant.

A Study of Incubation Aging of the Color Image on Multilayer Film Processed by Different Methods

N. I. Kirillov, A. M. Voĭtsekhovskaya, and N. E. Kirillova, pp. 240–245

An experimental study has shown that the character of incubation aging of a color-positive image obtained on processing a color-positive film by the original Agfa process (with a phosphate stop bath), by the process with two fixing baths, and by the NIKFI process is practically the same. The different changes in optical density and gamma of the different layers of the film which take place during aging put the image out of color balance and produce a marked fall in its quality which can be perceived visually. Hardening significantly decreases thermostatic aging. Unlike hardening in potassium alum solutions, hardening in formalin, in comparison with control samples, brings about an increase in the formation of new dye substances (reddish yellow fog) in the film. (*Translation of authors' abstract*)

The Problem of the Completion of Development of Multilayer Color-Negative Film

Ts. S. Arnol'd, pp. 246–252

In attempts at speeding up the NIKFI method of negative color processing for multilayer films, the results were not reproducible owing to the different degrees of "after-development" (continuation of development during washing) produced by inconstancy in the conditions of washing the film. The kinetics of after-development have now been studied in a number of solutions of salts of mineral acids and mixtures of them. After-development was found to proceed satisfactorily in these salts over a wide range of pH value (e.g. from 9.0–3.0). The author recommends that the water wash should be replaced by an after-development bath consisting of a 0.2% metabisulfite solution at a pH of 4.5. This is to be used after the diethyl-*p*-phenylenediamine developer in the NIKFI-3 process or the ethylhydroxyethyl-*p*-phenylenediamine developer in the NIKFI-4 process. This modified processing gives a somewhat lower film speed (about 20–30%) but the color fog is approximately halved, compared with that of normal processing.

The Problem of Conserving Developers

G. D. LITOVCHENKO AND S. A. SHIPITSYN, pp. 253–258

A study has been made of the use of stannous chloride (first suggested by Desalme in 1921) as a preservative in made-up developers. Two developers were studied, a Metol-hydroquinone and a *p*-aminophenol type, the latter showing the better keeping properties. When first added to the developer, the stannous chloride brought about some development in the unexposed parts of the emulsion, and some time was needed before treated developers began to behave normally. Developers with a preservative will develop a smaller area of emulsion than an equal volume of a normal developer, but the keeping properties are greatly enhanced.

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Résumés by S. Kikuchi and T. H. James

Progress in Photography in 1959

SHIN FUJISAWA (Research Lab., Fuji Photo Film Co., Minamiashigara machi, Kanagawa Pref.), pp. 107–112

Chemical Structure and Photographic Properties of s-Triazolopyrimidines [Tetrazaindenes]

SEIICHI OOBA AND KENZO SIRAKAWA (Research Laboratory, Fuji Photo Film Co., Minamiashigara machi, Kanagawa Pref.), pp. 113–118

The condensation product of ethyl acetoacetate and 3-amino-1,2,4-triazole, a well-known photographic stabilizer, is one of four possible isomeric substances, and some doubt existed as to its structure. The present authors show that it is 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene (*I*), as suggested by Bülow, and not 4-hydroxy-6-methyl-1,2,3a,7-tetrazaindene (*II*), as suggested by Birr. They synthesized Compounds *I*, *II*, and 4-methyl-6-hydroxy-1,2,3a,7-tetrazaindene (*III*) from 2-hydrazino-4-hydroxy-6-methyl-pyrimidine and formic acid, and showed that *II* can easily isomerize upon heating with formic acid to give *I*. (Similarly synthetic work has been reported by Allen, Beilfuss, Burness, Reynolds, Tinker, and VanAllan, *J. Org. Chem.*, *24*:787 (1959), who also established the identity of *I* with the condensation product of ethyl acetoacetate and the aminotriazole, and showed that *II* is converted to *I* by strong acid.)

Potentiometric titrations of 0.001 *M* solutions of *I*, *II*, and *III* indicate that 3 equivalents of silver ion are consumed. Details of the titrations are tabulated. Photographic tests were made on 100-gram samples of an iodobromide emulsion to which 1-, 2-, and 4-cc portions of 0.01 *M* solutions of the stabilizers were added before coating. The results of incubation tests for 5 days at 50°C and 80% RH indicate that the relative stabilizing power decreases in the order $III > I > II$.

Effect of Various Chemical Sensitizations on the β-Ray Sensitivity of Photographic Emulsions

SHINICHI KIKUCHI AND YASUSHI OISHI (Inst. Industrial Science, Tokyo University, Yayoicho, Chiba), pp. 119–122

The test emulsion was prepared from four solutions: (1) gelatin, 13.3 grams, distilled water, 185 cc; (2) potassium bromide, 15.4 grams, water, 30 cc; (3) silver nitrate, 20.0 grams, water, 30 cc; and (4) gelatin, 16.0 grams, water, 100 cc. All were maintained at 37°C. Solution (1) was added to 3 cc of Solution (3) and 0.5 cc of 2% hydrochloric acid, after which Solutions (2) and (3) were added simultaneously at the rate of 5.5 cc/min in an apparatus illustrated. Thirty minutes after these additions, Solution (4) was added, and the mixture was refrigerated to produce a gel. The gel was washed in running water for 2 hr at a temperature below 8°C. It was then sensitized by one of the following methods:

A. Sulfur sensitization. The emulsion was made alkaline by adding 3 cc of 1:4 ammonia to 380 cc of emulsion. A volume (0, 0.2, or 0.4 cc) of 0.01% allylthiourea solution was added to 100 cc of emulsion and the emulsion was ripened 1 or 2 hours at 60°C.

B. Reduction sensitization. The pH was adjusted to 5.8–6.0 and 0.3 or 0.6 cc of a solution of 50 mg of $SnCl_2 \cdot 2H_2O$, 0.5 cc of HCl, and water to make 100 cc was added to 100 cc of emulsion. The emulsion was ripened 1 or 2 hr at 60°C.

C. Sensitization by gold. For this sensitization, emulsions were prepared with Köpff 8835 gelatin and Nippi IN 101 gelatin. The aurous thiocyanate solution was prepared by adding 25 cc of 1% ammonium thiocyanate to 3 cc of 1% $HAuCl_4 \cdot 4H_2O$, and 0.4 cc of this solution was added to 100 cc of emulsion. Ripening time was 1 or 2 hr at 60°C.

D. Sensitization by triethanolamine. The sensitizing solution consisted of: triethanolamine, 13.5 grams, thymol, 0.5 grams, and ethanol to make 100 cc; 3.0–6.0 cc of this solution at pH 8.8 were added to 100 cc emulsion. Ripening time was 1.5 hr at 60°C.

E. Treatment with lead nitrate. In the preparation of the emulsion, 6.7 cc of 0.12% lead nitrate solution was added to the silver nitrate solution.

The emulsion samples were coated on glass and the plates were exposed to β-rays of S-35 or to light, then developed in D-19 for 5 min. The results are given as sensitometric curves. Sulfur and reduction sensitization gave about equal speeds to β-rays, although sulfur sensitization gave greater speed to light. Gold gave less sensitization to β-rays, and the speed was greater for Köpff gelatin than for Nippi for both β-rays and light. Triethanolamine sensitized to both β-rays and light. Lead ion, on the other hand, increased the sensitivity to β-rays but decreased the sensitivity to light.

A Rapid Spectrometric Method for the Determination of 1-Phenyl-3-pyrazolidone in Photographic Developers

EI TOJO, KAZUO KUROSAKI, AND MITSUO OZAWA (Research Lab., Fuji Photo Film Co., Minamiashigara machi, Kanagawa Pref.), pp. 123–127

The authors propose a method of analysis based on chloroform extraction, following the procedure of Levenson, but using the ultraviolet absorption at 247 mμ and the infrared at 1707 cm^{-1} to determine the amount of Phenidone in the extract. Since the solubilities of Phenidone and hydroquinone in chloroform at 20°C are 157.9 and 0.296 grams/liter, Phenidone can be extracted from P-Q developers without significant contamination by hydroquinone. The chloroform used must be of high purity to avoid possible complication by UV or IR ab-

sorption by impurities. The extraction is made at pH 5–6. Two substances extracted from the developer may interfere with the spectrometric determination: a decomposition product of Phenidone, and sulfur dioxide. The decomposition product, a hydrazine derivative with the formula C_2H_5N $(NH_2)C_6H_5$ has an absorption maximum at 270 mμ and correction is made for its presence in the extract from measurement of the absorption at this wavelength. The sulfur dioxide is removed from the extract by washing with a dilute solution of sodium bicarbonate.

The method is rapid and simple, requiring 10 min for the IR determination and 15–20 for the UV; the precision is ±0.01 gram in determining 0.5 grams/liter. The IR method is advantageous when the extract contains oxidation products or sulfur dioxide, since the absorptions of these agents are well separated from that of Phenidone in the IR region.

A Test of Rapid Processing in First Development of Coupler-in-Emulsion-Type Reversal Color Film

TAKUSHIRO TAKAGI (Technical Research Labs., Broadcasting Corporation of Japan (NHK), Tokyo), pp. 128–131

For special uses, such as in journalism and television, rapid processing may be indispensable in spite of some loss in quality. The author has made a preliminary study of the possibility of shortening the time of first development by using amidol. One formula tested is: anhydrous sodium sulfite, 100 grams; amidol, 30 grams; water to make 1 liter. Temperatures of 20°, 25°, and 30°C and times of treatment from 1 to 7 min were used. The time required for development could be reduced to 3 min at 30°, compared with the usual time of 15–20 min. The time of hardening after the first development has an important effect on the absorption spectra of the dyes, and curves are given for 0-, 2-, and 4-min hardening. The use of fluorescent lamps for the second exposure is suggested to minimize heating effects which would promote swelling in the emulsion.

Observation of Developed Silver Grain's Shape by Electron Microscope: I

HIDESABURO GENDA, TOMIYA SAKAGUCHI, AND SOUICHI KUBO (Faculty of Engineering, Chiba Univ., Iwase, Matsudo, Chiba Pref), pp. 132–136

The authors studied the form of the image silver developed in Fuji Process Plates by various developers: Metol, hydroquinone, *p*-phenylenediamine, diethyl-*p*-phenylenediamine, amidol, pyrogallol, catechol, and D-72. The individual agents were used in the formula: sodium sulfite, 0.5 grams; developing agent, 1.0 gram; sodium carbonate, 3 grams; water to make 100 cc. Spectral transmission curves and electron micrographs are reproduced. The images of the silver grains showed filaments for all developers, but some differences in fine structure were observed.

High-Level Radiation Dosimetry with Photographic Materials

YOSHITADA TOMODA, pp. 137–141

A review.

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Résumés by S. Kikuchi and T. H. James

The Role of Gelatin in Photographic Silver Halide Emulsions: II

HARUO IRIE (Chiba Univ., Iwase, Matsudo-shi, Chiba Pref.), pp. 56–62

A review (for Part I, see *P S and E*, 5:60).

Photographic Properties of Sensitive Materials for X-Rays: I — Some Properties of Developed Images Formed by Direct Irradiation

MATAICHI TAJIMA AND MINORU KATUMATA (Research Lab., Fuji Photo Film Co., Ltd., Minamiashigara-Machi, Kanagawa Pref.), pp. 63–70

The sharpness, graininess, and response function of some commercial materials used in x-radiometry were determined. The sensitive materials were: Fuji Industrial X-ray Films Types 80, 100, 200, and 400, Fuji Process Plate, and Fuji AI Plate. Characteristic curves are given for these materials exposed to 150-kv x-rays and developed in the specified developers. Graininess was measured by the blending distance method. Sharpness was determined from microphotometer traces of the developed image of a slit 0.15 by 0.55 mm in a copper plate 1.0 mm thick. Curves are given showing the dependence of sharpness on the measuring area of the microphotometer. The area adopted for the comparisons was 8 by 9 μ; further decrease in area produced little change in the sharpness values.

Graininess plots for some materials are given for both constant field brightness and constant illumination. The maximum graininess for constant illumination was obtained at density 0.4–0.7. The development time, for constant density, had very little effect on graininess. The higher the contrast, the sharper the image. The best sharpness was obtained with Type 200 Fuji Industrial X-ray film and finest grain with Type 80. The exciting voltage had a marked effect upon graininess and sharpness for voltages below 100 kv (decrease in voltage increased sharpness and improved grain), but little effect above 100 kv. The response function is plotted for several films.

Effects of pH of Gelatin Solutions on the Growth of Silver Bromide Crystals

AKIRA HIRATA (Chem. Research Lab., Konishiroku Photo Ind. Co., Ltd., Hinomachi, Tokyo), pp. 71–77

Several types of silver bromide suspensions were prepared by simultaneous addition (double jet method) over a period of 30 sec of 50 cc each of 2.95 *N* silver and 2.95 *N* halide solutions. An inert-type gelatin was used at 5 and 10% concentrations. Initial pH was adjusted at 3.5, 4.5, 5.5, 6.5, 8.5, and 10.5. The temperatures of addition and of physical ripening were 45°, 60°, or 75°C. The kinetics of grain growth for physical ripening times up to 128 min were studied by the turbidimetric method and optical photomicrographs of the grains were obtained. The shape of the crystals depended on the pH of the gelatin solution. At pH 3.5, thin flat well-shaped triangular or hexagonal crystals formed 80–90% of the total. The percentage, however, decreased with increasing pH, and the author attributes this to a change in the adsorp-

tion of the protective gelatin layer with change in pH. Increased pH favors the dissociation $-NH_3^+ \rightarrow -NH_2$; the adsorption of the gelatin to the crystals becomes weaker, favoring the occurrence of coalescence ripening at the high pH.

A series of experiments was carried out on the occurrence of coalescence ripening. Type I suspension was precipitated at pH 3.5, then, after 3 min, ripened for 128 min at pH 6.5 or 8.5. Type II was precipitated and ripened at pH 3.5. Type III was precipitated at pH 8.5, then, after 3 min, ripened for 128 min at pH 6.5 or 3.5. Type IV was precipitated and ripened at pH 8.5. The percentage of flat well-shaped crystals in Type I was nearly the same as in Type II, and the percentage in Type III nearly the same as in Type IV. These results suggest that coalescence occurs during and just after precipitation; after the crystals grow beyond the critical size, no further coalescence occurs.

Studies on Color Television Recording:
III—Photographic Photometry of Tricolor Images
IV—Relations Between Color Film and Color Television Camera
V—Desirable Characteristics of Color Film Used for Television

HIDESABUROU GENDA AND SOUICHI KUBO (Chiba Univ., Matsudo-shi, Chiba Pref.), pp. 78–88

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Résumés by S. C. Goddard

A Study of the Formation of Dyes in Black-and-White Development of Color Films

A. B. STREL'NIKOVA, I. I. LEVKOEV, AND N. I. KIRILLOV, pp. 6–13

In order to discover the effects of the black-and-white development which forms the first stage in color processing or which is carried out for the development of a sound track on color film, strips of color film, single-layer and multilayer, were exposed in a color sensitometer and developed in a number of black-and-white developers. After further processing including washing, fixing, and bleaching, the dyes formed in the strips by the reaction of the couplers with the oxidation products of the developer were examined. The developing agents studied were hydroquinone, Metol, amidol, and *p*-aminophenol.

Under these conditions yellow or magenta dyes were formed capable of affecting the color reproduction of the film. When the couplers were anilides of aroylacetic acid or derivatives of 1, 2-hydroxynapthoic acid without sulfonate groups in position 4, the tendency to dye formation was very marked. Addition of caustic alkali to the developer or reduction of the sodium sulfite concentration increased the tendency to dye formation. Some suggestions are made on the structure of the dyes formed in black-and-white development.

The Kinetics of Development of Separate Tracks from Ionizing Particles in Photographic Emulsions: II—The Kinetics of Development of Faded Tracks and the Fading of Development Centers

A. L. KARTUZHANSKIĬ, pp. 14–18 (For Part I, see *ibid*, 4: 417, 1959)

Studies were carried out on three emulsions with an average grain size of 0.25 μ, all obtained from a single parent emulsion but sensitized differently. They were sensitive respectively to 10–12 mev protons, 60-80 mev protons or 35–40 kev electrons, and to minimum-ionization particles. The radiations used were 5.3 mev α-particles (Po^{210}), 10 mev protons, 40 kev β-particles (from the β spectrum of Ca^{45}) and relativistic singly-charged particles of cosmic origin. The tracks were developed in ID-19 developer after different periods of keeping.

Development was observed to become slower, especially in the initial stages, as the time between irradiation and development was increased; this would indicate a decrease in the size of the development centers. Low-intensity reciprocity-failure studies show that the sensitivity centers are reasonably stable for the time between the irradiation and development, so that there is no change, during keeping, in the number of silver atoms required to form a development center and the changes in that number during keeping are calculated for the different forms of radiation. The general picture is very similar to that for development centers formed by light.

The Hypersensitization of Infrared Plates

I. I. BREĬDO AND A. A. MARKELOVA, pp. 19–26

Hypersensitization by water cannot be due solely to the decrease in concentration of bromide ions in the emulsion layer. In hypersensitization, side by side, with the washing out of bromide ions from the emulsion, there takes place a direct action of water (or ammonia) on the spectral sensitizers in the emulsion layer. It is most likely that this proceeds by the washing out of the oxidized molecules of the dye which are the cause of desensitization. As exposure is lengthened the efficiency of hypersensitization can be increased somewhat, in which case the increase is similar for the regions of natural and additional sensitivity and is connected with the decrease in reciprocity failure for the given emulsion. (*Translation of authors' abstract*)

The Calculation of the Limiting Sensitivity to Light of Photographic Materials

K. V. VENDROVSKIĬ AND V. I. SHEBERSTOV, pp. 27–33.

The maximum theoretical speed of an ideal photographic material is calculated mathematically. To start off with, the speed of a monolayer mosaic in which there is no free space between the grains and no overlapping, is calculated on the basis of the following assumptions: every quantum incident on any grain is absorbed; the absorption of one quantum is sufficient to make a grain developable; each developed grain is perfectly opaque. Speed is calculated as the reciprocal of the exposure required to give a standard density. Results tabulated range from a threshold speed of 2.6×10^{-8} (lux-sec)$^{-1}$ for a mosaic with 7 visual elements of continuous tone per millimeter, each containing 10 grains with an area of 2×10^{-5} sq cm, to 1.3×10^{-6} (lux-sec)$^{-1}$ for a mosaic with 100 visual elements per millimeter, each containing 100 grains with an area of 1×10^{-8} sq cm. Speeds calculated for a reference density of 1 range from 1.1×10^{-7} for the first case above, down to 130 for a grain size of 0.023×10^{-8} sq cm (the grain size of Eastman Kodak Microfile film). These calculations all refer to a light source of color temperature 5,000°K.

The more complex system of superimposed layers — still idealized but nearer to a practical emulsion layer — is considered and a theoretical speed of 6,700 (lux-sec)$^{-1}$ is obtained for a standard density of unity when 0.3 of the

total grains are developed, one photolytic silver atom forming the development center. If 0.9 of the grains are developed, the obtainable speed becomes 3160 (lux-sec)$^{-1}$. These calculations have all been made without taking into account any possible regression of the latent image or of reciprocity failure.

Anti-Repellency Activity and the Structure of Wetting Agents: IV—The Mechanism of the Anti-Repellency Activity of Surface Active Substances in the Coating of Photographic Emulsions

S. M. Levi and O. K. Smirnov, pp. 34–38

Three wetting agents chosen for their different capacities for preventing comet formation in photographic emulsion coating were studied as dispersing agents in an oil–water emulsion containing gelatin. The order of efficiency in comet prevention was the same as the order of efficiency for emulsification. The inference is that comet prevention takes place by the emulsification of small particles of fat or droplets of oil present in the emulsion.

The Kinetics of the Fixation of Photographic Materials

I. B. Blyumberg, V. G. Ivanova, A. E. Neĭman, and M. Ya. Pikus, pp. 39–49

Two different factors influence the kinetics of fixation of a silver halide layer by sodium thiosulfate: the diffusion of material into and out of the swollen layer, and the chemical reaction leading to the solution of the silver halide. If the first of these predominates, fixation should be accelerated by any process which would accelerate diffusion, while if the second were to predominate, any factor increasing the rate of solution would increase the rate of fixation.

Experiments show that in fact both types of factor have an influence on the rate of fixation. It is concluded that, in the majority of cases, the fixation of photographic materials is governed by a mixed type of kinetics. Diffusion tends to dominate at small concentrations of silver solvent and also with large emulsion thicknesses, while chemical kinetics predominates in thin layers with a small content of silver halide in fixers with a large or average concentration of thiosulfate. Other experiments show the effect of swelling and hardening of the layer on fixation. The mechanism of fixation is complex and possibly is not completely covered by the processes of diffusion and solution.

The Application of High-Speed Cinematography to the Study of the Destruction of Rock

S. R. Zhukovskiĭ, M. Fal'kon, and R. M. Eĭgeles, pp. 50–52, 1 plate

The breaking of rock under the action of a chisel or similar tool cannot be studied directly by means of high-speed cinematography, so a glass block has been used as a transparent model. The propagation of cracks under the influence of a blow took place so rapidly that frame frequencies of the order of 100,000/sec were needed, and consequently the Russian FP-22 camera, capable of such speeds, was used.

Objective Distortions of Cinematograph Images with Vertical and Horizontal Projection Angles: II—The Cylindrical Screen

E. M. Goldovskii and S. S. Ryshkov, pp. 53–60

The mathematical analysis of distortions introduced into the projected picture by the angle of projection, carried out for a flat screen in Part I (*Zhur. Nauch. i Priklad. Fotografii i Kinematografii*, **5**: 439–45 (1960)), is here extended to the case of the cylindrical screen.

The Determination of the Iron and Manganese Content of Photographic Developers

I. R. Klyachko, A. D. Vinogradova, and M. E. Koval'skaya, pp. 61–62

Two spot reactions capable of quantitative interpretation are used for the analysis of metals in developer solutions. Iron is estimated by the reaction with potassium thiocyanate, and manganese by the color reaction with sodium bismuthate.

The Influence of Atmospheric Humidity on "After-Hardening" of Photographic and Gelatin Layers

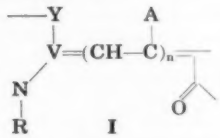
V. L. Zelikman, p. 63

Gelatin layers containing chromium acetate as a hardener were stored in an incubator at 50°C under different atmospheric humidities. The melting point of the gelatin rose rapidly on keeping in a relative humidity of 100%, not at all at 16%, and slightly at 53%. The sample stored at 16%, when transferred to an atmosphere of 100% RH behaved like the sample which had been placed directly in the 100% RH atmosphere. No significant lowering of melting point was observed when a sample conditioned at 100% RH was transferred to an atmosphere of 16% RH.

The Character of the Spectra of Sensitization and Absorption of Some Dimethinemerocyanines in Emulsion

E. B. Lifshits, pp. 64–66

Spectra of sensitization and absorption (in silver iodobromide emulsions and on silver bromide preparations) have been obtained for di- and polymethinemerocyanines derived from different ketomethylene compounds, in particular from 3-alkylrhodanine and thionaphthen-3-one, differing in the nature of the nitrogen-containing heterocyclic residues of structure **I**.



I

(Y is O,S,Se, —CH=CH—, $C(CH_3)_2$, NR, etc.; V is =C—, or —C=C—C=; n is 1,2, or 3; A is H or, for $n=1$, A is H,CH_3, C_2H_5 or OC_2H_5; R is alkyl).

From the structure of the spectra, it is concluded that, contrary to the usual opinion, merocyanines derived from unsymmetrical cyclic ketomethylene compounds have an inherent tendency to J-aggregation.

Methods of Raising the Effective Sensitivity of the Photographic System

K. V. Chibisov, pp. 67–74

For English translation of this article, see *J. Phot. Sci.*, **9**:26-35 (1961).

Third International Conference on Nuclear Photography

K. S. Bogomolov, pp. 75–77

The Conference proceedings are briefly reported.

• New Products and Developments

FRANK SMITH

• Cameras and Accessories

Benson-Lehner High-Speed Stereo Camera

Benson-Lehner Corp., Santa Monica, Calif., has announced the Stereoflex, a stereo high-speed camera which was developed for a special Navy project, but has application in many fields of research. The camera uses special 35mm film, and magnifies 1 sec of action to 1 min of viewing. The rotating-prism camera can accelerate the film to running speed in less than 1 sec, and then hold a steady speed.

Kinoptik 197° Wide-Angle Lens

Karl Heitz Inc., 480 Lexington Ave., New York 17, is the U.S. distributor for the Kinoptik 1.9mm $f/1.9$ Lens (in C-mount) for motion-picture and television cameras. The new lens is a 9-element apochromat with an extreme wide-angle coverage of 197°, giving a round image (8.7 mm in diameter), and actually photographing an area behind the photographer.

Oscilloscope Camera

The Model SM-209 Scope Camera, developed by the Electronic Tube Corp., 1200 E. Mermaid Lane, Philadelphia 18, Pa., uses the Polaroid-Land Camera Back in a special sliding mount which permits up to nine different trace exposures per print. Aperture, speed, and focus adjustments can be made without reaching through access doors or removing the camera from the scope.

The camera is equipped with an $f/1.9$ Wollensak Oscillo-Raptar 75mm coated anastigmat lens, designed specifically for high-resolution oscilloscope photography. Object-to-image ratio is 1:0.9, and a calibrated focusing scale allows the camera to be used on many different scopes.

• Illumination

Piezoelectric Power Source for Photoflash Lamps

U.S. Patent 2,972,937, dated Feb. 28, 1961, issued to Chauncey G. Suits, Schenectady, N.Y., assignor to General Electric Co., claims a power source consisting of a piezoelectric crystal arranged to provide a conducting path to the terminals of a photoflash lamp, and a mechanical arrangement for deforming the piezoelectric crystal in synchronized relation to the opening of a camera shutter. The deformation, which may be accomplished either by striking the crystal a sharp blow or by releasing the pressure on a prestressed or preloaded crystal, produces the electrical energy required to flash the lamp. The inventor states that a crystal of barium titanate will yield a voltage of 200 to 1,000 for a duration of a few microseconds with a total energy in the order of microwatts. A barium titanate piezoelectric crystal of about $\frac{1}{8}$ in. diameter and $\frac{1}{8}$ in. thickness will yield a potential of about 450 v and has been employed satisfactorily for this purpose.

It is particularly advantageous to employ a low-energy-initiated lamp of the type described in U.S. Patent 2,868,-003. It will be seen that the piezoelectric crystal arranged according to the present invention and synchronized with a camera shutter, either by a cable release or by incorporation of the crystal into the shutter mechanism has very attractive features as a batteryless flashlamp igniter. The crystal has a long life and is extremely reliable, and the combined shutter mechanism, crystal, and associated deforming mechanism may be assembled as a complete unit for use with many different types of cameras.

EG&G Light Source for Optical Maser

Edgerton, Germeshausen and Grier, Inc., 160 Brookline Ave., Boston 15, Mass., has developed a high-energy light source for optical masers. Called the Model 511 Laser Stimulator, the source is the result of work done by Dr. H. E. Edgerton. Close optical coupling between the flashtube and the crystal and the use of special U-shaped xenon-filled flashtubes make possible an increase in the efficiency of the light source by a factor of about 10 over that of the conventional spiral flashtube.

The flashhead contains from 4 to 10 flashtubes, depending on the light requirements and the diameter of the crystal used. Each tube is conservatively rated at 100 wsec/flash. Crystals approximately 2 in. long and up to $\frac{1}{2}$ in. in diameter can be accommodated. Tube holders can be relocated, when necessary, to increase the space between the flashtubes and the crystal, permitting forcing of a coolant around the crystal. A blower is incorporated in the flashhead for air cooling of the assembly. Flashtubes may be connected in series or in series parallel.

The flashtube assembly is enclosed in a degreased aluminum-foil cover which deflects a maximum of light upon the crystal. The complete unit is then housed in a metal case. The energy storage bank has a capacity of 160 μf which can be connected to equal 80 μf. Maximum output is 1280 wsec at 160 μf. An auxiliary capacitor bank can be added in parallel to increase the output. Minimum recycling time is 2 sec. Flash rate is determined by the characteristics of the crystal and the flashtube. Power requirements are 110 or 220 v, 60 cycle, 2 kw, and total weight is 300 lb.

Although the information contained in this section is compiled from sources believed to be reliable, the author cannot assume responsibility for its accuracy. Publication of the information here is not to be construed as an endorsement or recommendation of the product or equipment described.

• Processing

Eastman Viscomat Processor

A rapid processor for professional use that can process 16mm black-and-white motion-picture positive, sound-recording, and television recording films at camera speed of 36 ft/min has been announced by the Eastman Kodak Company, Rochester, N.Y.

The Viscomat Processor, Model 10P, uses viscous solutions, applied at 125°F and maintained at this temperature in a water-saturated atmosphere. As the film enters the processing compartment, it passes an extrusion hopper that uniformly applies a thin layer of the viscous developer to the emulsion surface. At the completion of development, which can be varied from 2½ to 7 sec, the developer is flushed off the emulsion with jets of 130°F water. A Venturi-type squeegee removes the surface water, and the viscous fixer is then spread onto the emulsion by another extrusion hopper. When fixing is complete, a hot-water spray wash is used, followed by a second Venturi-type squeegee and warm-air drying. One frame of film is completely processed in 1 min.

The processing baths are supplied in ready-to-use form, and the only external services required are electricity and hot water.

The processor occupies a floor space of 16 by 21¼ in., and it is claimed to produce film quality as good as that obtained with conventional professional motion-picture processors.

Houston Processor for Kodachrome II Film

The Houston Model 515-K2 continuous processor was designed by the Houston Photo Products Div., Houston Fearless Corp., Burbank, Calif., to process Kodachrome II Film in 8/16 and 35 mm widths. Either one strand each of 8/16 and 35mm film or two strands of 8/16 mm film can be processed simultaneously.

Independent drive systems for the two film sizes are on opposite sides, but utilize the same solution tanks and drying cabinet. A single all-purpose drive shaft on the bottom controls film tension. Speeds are 12½ ft/min for 8/16 mm and 5 ft/min for 35 mm.

The processor is equipped with automatic on–off switch, loading elevators, pumps, replenisher tanks, compressor, air filters, and control panel. Automatically controlled heating and refrigerating equipment is also standard. The processor is 5 ft high by 16 ft long and requires no platform.

• Projection

Flicker-Free Variable-Speed Projector

L-W Photo Products Co., Northridge, Calif., is now producing the L-W Photo-Optical Data Analyzer, a 16-mm projector which permits variable-speed projection from still to 24 frames/sec without flicker. Designed for data reduction of instrumentation film, the projector provides unlimited single-frame hold time, effective cooling that prevents film damage, and complete control of speed and direction.

A daylight viewer is built in for desk-top analysis. An attached frame counter adds and subtracts, and can be reset to zero. Additional features include fast rewind, film-framer and elevating control, simplified threading, and convenient storage capacity. The projector is equipped with a 2-in. *f*/1.6 coated lens with field flattener, and a 750- or 1000-w prefocused base-down projection lamp. Film capacity is 400 ft, and the power required is 105-125 v ac. Dimensions are 2½ by 14 by 10¾ in. and the weight is 26 lb.

• Radiography

Zenith Pulsed X-Ray System

Zenith Radio Research Corp., Menlo Park, Calif., has announced development of a pulsed x-ray system with the ability to make cineradiographs of high-speed phenomena in 1μsec or less. The system consists of two compact units: a console containing the x-ray generating tube, its power supply and control circuits; and an image intensifier console.

The oxide-coated thermionic hot-cathode x-ray tube is capable of conducting high currents at high voltage with fast rise-time characteristics. With a life in excess of some million shots, the tube was proven in tests to have excellent reproducibility of pulse length, voltage, current, and consequently, x-ray output. The company states that prior to development of the Zenith tube, high-intensity x-ray tubes were limited to a life of several hundred shots, frequently possessed unreliable pulse characteristics, and could be pulsed only once every several minutes.

The x-ray tube is pulsed with a square-wave voltage pulse 1 μsec in duration at a rate which is continuously variable from 1 to 30 pulses per sec. Amplitude of the voltage is continuously variable from 0 to 150 kv. When the tube is operated at 150 kv with a beam current of 130 amp, the x-rays are generated by an electron beam of approximately 20 megawatts focused on the x-ray conversion target. The resulting high-intensity x-rays have an effective spot size of 1 to 2 mm throughout the life of the tube, and at 1 in. from the target have an intensity rate of 10^7 r/sec.

The high-powered, short pulses of x-radiation are passed through the subject under study and impinge on the screen of the image-intensifier tube, which amplifies the x-ray image and converts it to visible light. The image can be viewed directly, transmitted by closed-circuit television, or photographed. The light intensity is sufficiently high to permit the use of fine-grain film for motion-picture recording.

An additional feature of the equipment is that a single 1 μsec x-ray pulse has sufficient energy to permit a radiograph to be taken directly on conventional film. Adequate film density is obtained from a single pulse through 1½ in. of aluminum at a distance of 6 ft from the x-ray tube.

• Reproduction and Copying

Automatic Document Copying Machine

An automatic copying machine using the diffusion transfer process has been introduced under the names Amptomatic, Transcopy Automatic, Cormac 66, and Contura Executive, by the four marketing subsidiaries of Anken Chemical and Film Corp., Newton, N.J.; under the name Transfer-a-matic, by Ozalid Division of General Aniline and Film Corp., Johnson City, N.Y.; and under the name Consector, by Photek, Inc., Providence, R.I.

The machine copies any kind of original up to 11 in. wide and 150 ft in length. It automatically turns itself on when an original is fed into it, makes the exposure, adjusts itself to the length of the original, trims the positive, delivers the developed print flat and dry, produces at a rate of 4 copies per min, and turns itself off. It is re-

ported to make clear black-and-white copies of all colors, produce high-quality permanent copies, and give a useful copy every time.

The housing for the copier is 22 in. wide, 18 in. deep, and 10 in. high, and is molded of high-impact polystyrene. It weighs 65 lb and operates on standard 115 v ac.

Larger Kodak Verifax Copier

A semi-automated Verifax copier, for volume reproduction of engineering documents and other papers up to 11 by 17 in., has been introduced by the Eastman Kodak Company, Rochester 4, N.Y.

To accommodate a wide range of engineering documents, the larger model accepts matrix sheets 11 by 17 in., 8½ by 14 in., or 8½ by 11 in. In addition to standard A & B size drawings, it will copy operations sheets, parts lists, standard data sheets, etc. Translucent masters can be made from opaque or translucent originals for use on diazo machines.

The unit is 24 by 23 by 14 in., and weighs 41 lb. It holds up to 100 sheets of copy paper. A copy paper tray with side guides and backstops capable of handling letter, legal, and 11 by 17 in. copy paper is provided with the copier. Quick size change may be achieved with a single lever. A simple accessory tray is available for handling translucent and card-weight copy paper with 2-in. "tabs." An 11- by 17-in. Verifax Matrix Dispenser is supplied with the unit.

• Sensitive Materials

Kodak Films for Aerial Mapping

Three aerial photographic films for topographic mapping have been announced by the Eastman Kodak Company, Rochester 4, N.Y. The new films are made with an Estar polyester base that provides high strength and excellent dimensional stability. They have a gelatin backing to reduce curl and protect against static, and both the gelatin backing and the film emulsion itself are hardened for high-temperature rapid processing.

Because both film base and photographic emulsion are thinner in the new films, drying time is shorter, and more exposures can be made on a roll of the new film than could be made on a roll of acetate-base film of the same diameter.

Films coated on the new 0.004-in. Estar base are Kodak Experimental Panatomic-X Aerographic Film (Estar Base), Kodak Experimental Plus-X Aerographic Film (Estar Base), and Kodak Experimental Tri-X Aerographic Film (Estar Base). The emulsions cover a wide speed range and are improved versions of emulsions used previously on acetate-base film.

• Miscellaneous

Itek Photographic Data-Processing and Retrieval System

Itek Laboratories, Lexington, Mass., has developed an automatic film-handling system which will process, index, reproduce, and display 70mm high-resolution panoramic aerial photographs. The ground-handling system is capable of converting opaque copy and 35mm strip film into a single-unit record size called the center format. This center format can then be duplicated, processed, viewed, or prepared for other purposes.

The center format, which can be either a photographic negative or positive is divided into two general regions, the accession number region, and the information storage area. The format is composed of two types of accession numbers, a ten-digit human-readable number, and a corresponding machine-readable number, each of which is expressed in a four-bit binary code. The information area is used to store photographically the information provided by the inputs mentioned above.

The first phase of operation is the conversion of input material into center formats. This is accomplished by the Photographic Projection Printer EN-65, the Copying Camera KE-29, and the Photographic Projection Printer EN-62. The outputs of these units are exposed center-format negatives. Because these negatives must be converted into positives in order to be projected, positive duplicates are made in the Contact Printer EN-63.

In the third phase of operation, the center-format positives are placed in the Photointerpretation Console OA-2270, a machine which aids photointerpretation by providing variable magnification, rectification, and comparison viewing. In addition, material can be prepared for agencies outside the photointerpretation center by the Photographic Projection Printer EN-64. This machine accepts center-format negatives, and converts them to 9½ by 18½ in. positive transparencies or enlarged paper prints.

FileSearch System for Storage and Retrieval of Information

A machine which can automatically search a 32,000-page file at the rate of 6,400 pages/min, and present the desired information for viewing or printing copies, has been developed by FMA, Inc., El Segundo, Calif.

The FMA FileSearch System is composed of a recording unit and a retrieval unit. The recording unit photographs files of documents along with a description of each document's contents, which is coded in the form of opaque spots. These are stored together on reels of microfilm. The system stores 32,000 8½- by 11-in. pages on a single reel of microfilm, and can accommodate over 1,600,000 pages of information, enough to crowd 40 four-drawer file cabinets, in a single file cabinet.

When information is desired, up to six requests on punched cards may be fed simultaneously into the machine, whereupon the machine will automatically search the microfilm reels, making copies of the requested material.

Avscan Infrared Scanning Device

Development of an infrared scanning device so sensitive that it forms a picture of a human being merely by picking up heat emitted from his body has been announced by Avco Corp., Electronics and Ordnance Div., Cincinnati 15, Ohio. The device may be used to detect enemy missiles or airplanes.

The unit consists of a scanning head, a signal processing unit, a display unit, and a cryogenic cooling unit. The scanning head includes a refractive optical system consisting of four infrared achromat lenses mounted on a rotating drum. These lenses scan with a resolution of 0.1° by 1°. The rotating optical system is mounted behind a 6½-in. protective dome.

The detector is mounted in a side-looking metal dewar, and is cooled with liquid nitrogen to −196°C. The infrared cell is an indium antimonide junction type.

Nord Microfilm Video Transmission System

Television Utilities Corp., Div. of Nord, 300 Denton Ave., New Hyde Park, N.Y., has announced a system for transmitting microfilm images to remote areas. A microfilm slide is scanned by a beam of light emanating from a cathode-ray tube, and the modulation of the beam

produced by the image on the slide is converted to an electrical signal by a photocell. The amplified signal is mixed with synchronizing impulses to lock the outgoing "picture" in step with the transmitter. This composite signal is then fed into coaxial cable and distributed to any number of locations where the picture is reproduced on display tubes. For greater clarity and detail, the system uses 945 scan lines/frame compared with 525 used in commercial television.

Glossaries of Photographic and Optical Terms

The *Glossary of Photographic Terms*, recently approved for publication by the U.S. Government Printing Office as Military Handbook MILHDBK 25, was compiled by the U.S. Army Signal Material Support Agency, Fort Monmouth, N.J. It contains some 2,713 precisely defined photographic terms, and provides an authoritative and uniform guide for the Armed Forces and defense contractors. It is expected that its use in specifications, standards, and other government documents will promote a more accurate interpretation of requirements. The glossary is the culmination of some two years of work, and was produced with the cooperation of the Navy, Air Force, industry, and many scientific and technical institutions and associations.

The *Glossary of Terms Frequently Used in Optics and Spectroscopy*, by Alva H. Bennett, American Optical Co., published by the American Institute of Physics, is a useful and convenient compilation. The glossary is not intended to be critical, definitive, or authoritative, but is rather a layman's guide in the field. Nevertheless, it will prove worth-while to anyone interested in the subject and constitutes a valuable addition to the existing literature.

IRE Standard on Electrostatographic Devices (60IRE28.S2)

The new standard on electrostatographic devices, approved by the IRE Standards Committee, April 14, 1960, as 60IRE28.S2, is reproduced below in its entirety by permission of the Institute of Radio Engineers, 1 E. 79th St., New York, N.Y.

DEFINITIONS

Aerosol Development. Development by means of a suspending gas.

Cascade Development. Development by means of gravitational forces.

Charging (*Electrostatography*). See *Sensitizing.*

Corona Charging. Sensitizing by means of gaseous ions generated by corona ionization.

Development (*Electrostatography*). The act of rendering an electrostatic image visible in which the image-forming material is carried to the field of the electrostatic image, as by a fibrous brush, a suspending liquid, or other means.

Electrographic Recording (*Electrostatography*). That branch of electrostatic electrography which employs a gaseous discharge between two or more electrodes to form directly electrostatic charge patterns on an insulating medium for producing a visible record.

Electrostatic Electrography. That branch of electrostatography which employs an insulating medium to form, without the aid of electromagnetic radiation, latent electrostatic charge patterns for producing a visible record.

Electrostatic Electrophotography. That branch of electrostatography which employs a photo-responsive medium to form latent electrostatic images with the aid of electromagnetic radiation for producing a visible record.

Electrostatography. The formation and utilization of electrostatic charge patterns for the purpose of recording and reproducing patterns in visible form.

Exposure (*Electrostatography*). The act of subjecting a photoconductive insulating medium to electromagnetic radiation.

Fixing (*Electrostatography*). The act of bonding a developed image to a supporting member, as by the use of heat, solvent, or mechanical pressure.

Magnetic Brush Development. Development by means of ferromagnetic particles as carriers under the influence of a magnetic field.

Sensitizing (*Electrostatography*). The act of establishing an electrostatic surface charge of uniform density on an insulating medium.

Transfer (*Electrostatography*). The act of moving a developed image, or a portion thereof, from one surface to another without altering its geometric configuration as by electrostatic forces or contacting with an adhesive coated surface.

Xerography. That branch of electrostatic electrophotography with employs a photoconductive insulating medium to form latent electrostatic images with the aid of infrared, visible, or ultraviolet radiation for producing a visible record.

Xeroprinting. That branch of electrostatic electrography which employs a pattern of insulating material on a conductive medium to form electrostatic charge patterns for duplicating purposes.

Xeroradiography. That branch of electrostatic electrophotography which employs a photo-conducting insulating medium to form latent electrostatic images with the aid of x-rays or gamma rays for producing a visible record.

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